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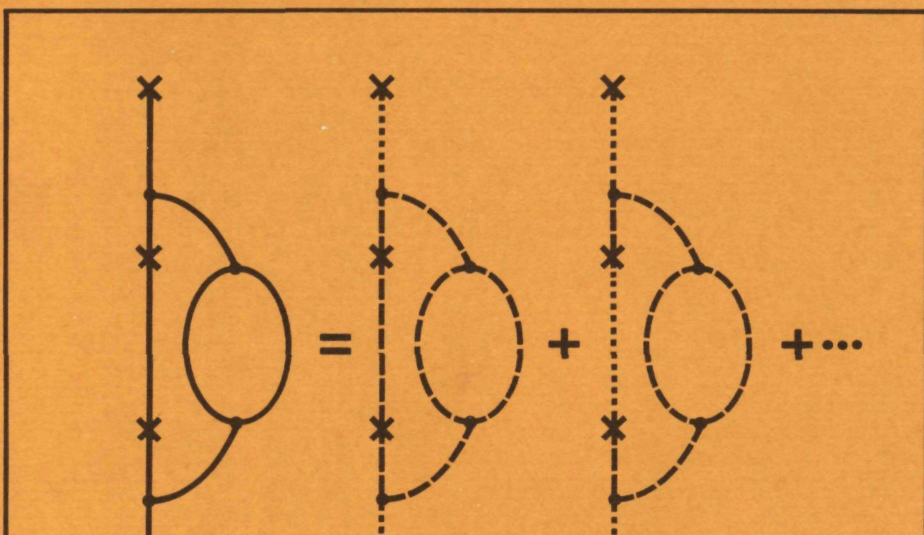
generalized hydrodynamics for the diffusion process



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GENERALIZED HYDRODYNAMICS
FOR THE DIFFUSION PROCESS

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GENERALIZED HYDRODYNAMICS FOR THE DIFFUSION PROCESS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
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en mijn ouders

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CONTENTS

INTRODUCTION

In this dissertation the diffusion of one particle in a classical fluid of identical particles is studied theoretically. This phenomenon is known as the self diffusion process.

Theoretically the self diffusion problem is interesting since it is the simplest transport process occurring in a fluid and it contains many of the general aspects of non-equilibrium phenomena.

Experimentally it can be studied in several ways.

The dynamical properties (such as the mean square displacement) of a particle in a bath of mechanically equivalent particles can be measured by means of tracer diffusion experiments.

The self diffusion process is involved in the explanation of incoherent neutron scattering experiments on simple fluids.

It describes (approximately) the diffusion of binary mixtures provided the mechanical interactions between the particles of both species are (almost) identical.

The last ten years it has become possible to study the dynamics of a hard sphere system by means of computer experiments.

We will study the self diffusion process theoretically by means of a function $G(\vec{r},t)$, which is the probability of finding a tagged particle at time t at the position $\vec{r}$ when it was initially at the position $\vec{r}=o$.

In general, dynamical properties of simple fluids near equilibrium are described by phenomenological hydrodynamic equations (i.e. the Navier Stokes equations). For self diffusion the hydrodynamic equation involved is known as the diffusion equation or Fick's law,

$\partial G(\vec{r},t)/\partial t = D\, \vec{\nabla}^2\, G(\vec{r},t)$, and the proportionality constant D is the self diffusion coefficient.

The main purpose of this dissertation will be the derivation and extension of the hydrodynamic equation for the diffusion process (i.e. Fick's law) on the basis of a microscopic theory.

Usually such an investigation can be made on the basis of the Boltzmann equation, the main properties of which are discussed here.
The basic assumption to derive the Boltzmann equation is that successive collisions between the particles are *uncorrelated*, and therefore the theory is supposed to be valid for low densities. The predictions are the following.
There are two well separated time scales involved in dynamical processes, a kinetic time scale t_o , in which the one particle distribution function decays to local equilibrium, and a hydrodynamic time scale t_H , much larger than t_o , in which the state close to local equilibrium decays to over all equilibrium. Here t_o is on the order of the mean free time between collisions and t_H is a typical relaxation time for local density disturbances of the system.
The velocity correlation function of a tagged particle $< \vec{v}_1 \cdot \vec{v}_1(t) >$, where $< \dots >$ denotes an equilibrium average, is a fastly decaying function of time when measured on the time scale t_o . This is due to the fact that the order of magnitude of the collision term in the Boltzmann equation is typically on the order of the collision frequency (t_o^{-1}) .
The probability distribution function $G(\vec{r},t)$ fulfills approximately Fick's law on the hydrodynamic time scale (i.e. $t \gg t_o$) . The Boltzmann equation predicts that Fick's law can be improved by taking higher spatial derivatives of $G(\vec{r},t)$ into account introducing new proportionality constants, which are known as the Burnett, super Burnett, ... , coefficients (for self diffusion the Burnett coefficient is absent due to symmetry).

It was generally believed that these properties, which follow from the Boltzmann equation, are also valid for general fluids. However Alder has shown from computer experiments that the velocity correlation function is *not* a fastly decaying function of time, but decays as a power law for times much larger than t_o .
It became clear from theory and experiment that these "long time tails" are due to many body processes, which contain persistent memory effects arising from sequences of *correlated* binary collisions.
The long time tail in the velocity correlation function indicates that the kinetic and hydrodynamic time scales in dynamical processes are not well separated.
In view of these facts we reconsider the derivation and study possible extensions of Fick's law.

In this dissertation we employ two theories, which are capable to predict the long time tail in the velocity correlation function.
They are:

- Kinetic theory of hard spheres at low densities, which is a microscopic theory derived from the Liouville equation.
- Mode coupling theory, whose derivation is based on phenomenological arguments. It is not restricted to low densities or hard core interactions.

By means of kinetic theory we study extensively two quantities, the time dependent diffusion coefficient, which in fact is the time integral of the velocity correlation function, and the time dependent super Burnett coefficient.
If the time dependent diffusion coefficient tends to a constant for large times, this limiting value is by definition the self diffusion coefficient and Fick's law is confirmed.
If the time dependent super Burnett coefficient is finite for t tending to infinity the phenomenological super Burnett coefficient exists and the extension of Fick's law by taking higher derivatives of $G(\vec{r},t)$

into account is meaningful.
As was already discussed in recent literature one finds from kinetic theory that Fick's law exists in three dimensional systems, and does not exist for two dimensions.
We will show from kinetic theory that also the super Burnett coefficient does *not* exist, both in two *and* three dimensions.
The mode coupling theory in three dimensions will be used to extend the previous results to fluid densities and to generalize the diffusion equation beyond Fick's law in a meaningful way.

In chapter I we consider the quantities of interest in the self diffusion problem and discuss how Fick's law can be obtained as a limiting case of exact relations.
Chapter II is devoted to kinetic theory of hard spheres at low densities. A derivation will be given starting from the Liouville equation and applying standard diagrammatic techniques. The results of chapter II will be used to calculate the time dependent diffusion and super Burnett coefficient in three dimensional (chapter III) and two dimensional systems (chapter IV).
Chapter V is devoted to the mode coupling theory, where the same quantities are calculated for fluid densities, and where Fick's law is generalized to include higher order gradients of $G(\vec{r},t)$.
The results of chapter III have already been published (De Schepper 1974).

CHAPTER I

The Self Diffusion Process

a. *Definitions*

In this chapter we consider the quantities describing the self diffusion of a tagged particle in a classical fluid of identical particles without internal structure and interacting with central pairwise additive forces both in two and three dimensions.
Exact relations are derived between the quantities of interest and we discuss a method to obtain the phenomenological linear self diffusion equation (i.e. Fick's law) and its predictions for various quantities, as limiting cases of the exact relations.

We consider a classical system of N identical particles of mass m in a d dimensional box of volume V, with periodic boundary conditions and a Hamiltonian

$$H(\Gamma) = \sum_{i=1}^{N} \tfrac{1}{2} m v_i^2 + \sum_{\alpha} \Phi(r_\alpha) \ , \qquad (I.1)$$

where α runs over all pairs (i,j) of different particles in the system and $r_\alpha = |\vec{r}_\alpha| = |\vec{r}_i - \vec{r}_j|$ is the distance between the particles i and j. The spatial and velocity coordinates of particle i are denoted by $\vec{r}_i$ and $\vec{v}_i$ while Γ denotes the phase point $\Gamma = (\vec{r}_1, \vec{v}_1, \ldots, \vec{r}_N, \vec{v}_N)$. The particles move according to Hamilton's equation of motion such that for any phase function $f(\Gamma)$, which does not depend explicitly on time

$$\frac{\partial}{\partial t} f(\Gamma(t)) = L \, f(\Gamma(t)) \ . \qquad (I.2)$$

The formal solution reads

$$f(\Gamma(t)) = S_t \, f(\Gamma(o)) \,, \qquad (I.3)$$

where S_t is the streaming operator replacing the coordinates of the particles at time t=o , $\Gamma(o)$, by their values at time t , $\Gamma(t)$, and can formally be written as

$$S_t = \exp(tL) \,. \qquad (I.4)$$

The Liouville operator L is defined by the Poisson Brackets $L\, f(\Gamma) = \{ f(\Gamma), H(\Gamma) \}$ and explicitly given by

$$L = \sum_i L_o(i) - \sum_a \Theta_a \,, \qquad (I.5)$$

where i runs over all particles and a over all different pairs of particles and

$$L_o(i) = \vec{v}_i \cdot \frac{\partial}{\partial \vec{r}_i} \,, \qquad (I.6)$$

$$\Theta_{ij} = \frac{1}{m} \frac{\partial \Phi(r_{ij})}{\partial \vec{r}_{ij}} \left(\frac{\partial}{\partial \vec{v}_i} - \frac{\partial}{\partial \vec{v}_j} \right) . \qquad (I.7)$$

The sum $\Sigma\, L_o(i)$ is called the free streaming part of the Liouville operator and $\Sigma\, \Theta_a$ the interaction part. The tagged particle is taken to be particle number 1 .

In the self diffusion process of a tagged particle one is interested in the probability $P(\vec{r},t)$ of finding the tagged particle at time t at the position $\vec{r}$, if the initial probability at time zero is a given function $W(\vec{r})$ i.e.

$$P(\vec{r},o) = W(\vec{r}) \,. \qquad (I.8)$$

The probability $P(\vec{r},t)$ can be expressed as a non-equilibrium average of the microscopic tagged particle density $\delta(\vec{r}_1-\vec{r})$

$$P(\vec{r},t) = \int d\Gamma\ \rho(\Gamma;t)\ \delta(\vec{r}_1-\vec{r}) \ . \qquad \text{(I. 9)}$$

Here $\rho(\Gamma;t)$ is a normalized non-equilibrium ensemble satisfying Liouville's equation

$$\frac{\partial}{\partial t}\rho(\Gamma;t) = -L\ \rho(\Gamma;t) \qquad \text{(I.10)}$$

and can therefore be written as $\rho(\Gamma;t) = S_{-t}\ \rho(\Gamma;o)$. Due to Liouville's theorem, (I. 9) may be written as

$$P(\vec{r},t) = \int d\Gamma\ \rho(\Gamma;o)\ \delta(\vec{r}_1(t)-\vec{r}) \ .$$

The initial ensemble $\rho(\Gamma;o)$ has to be determined from the initial condition $P(\vec{r},o) = W(\vec{r})$. For experimental situations where all other macroscopic variables such as pressure, temperature and total density are uniform throughout the system, the simplest choice for $\rho(\Gamma;o)$ is (Dorfman 1974)

$$\rho(\Gamma;o) = \frac{VW(\vec{r}_1)}{Z(T,n_o)}\ e^{-\beta H(\Gamma)} \ , \qquad \text{(I.11)}$$

where $Z^{-1}\exp(-\beta H)$ is the normalized canonical equilibrium distribution function at temperature T and total density $n_o = N/V$ and $\beta = (k_B T)^{-1}$ where k_B is Boltzmann's constant.
The choice (I.11) for the initial ensemble yields

$$P(\vec{r},t) = \int d\vec{r}\,'\ \tilde{\tilde{G}}(\vec{r}-\vec{r}\,',t)\ W(\vec{r}\,') \ , \qquad \text{(I.12)}$$

where $\tilde{\tilde{G}}(\vec{r},t)$ is given by

$$\tilde{\tilde{G}}(\vec{r},t) = V < \delta(\vec{r}_1(o)-\vec{\rho})\ \delta(\vec{r}_1(t)-\vec{\rho}-\vec{r}) >$$

$$= < \delta(\Delta\vec{r}_1(t)-\vec{r}) >$$

$$= Z^{-1} \int d\Gamma\ \exp(-\beta H(\Gamma))\ \delta(\Delta\vec{r}_1(t)-\vec{r})\ . \qquad (I.13)$$

Here $\Delta\vec{r}_1(t) = \vec{r}_1(t) - \vec{r}_1(o)$ is the displacement of the tagged particle and the brackets $< \ldots >$ represent the canonical equilibrium average. It is tacitly assumed that quantities like $\tilde{\tilde{G}}(\vec{r},t)$ are actually the thermodynamic limit ($N\to\infty$, $V\to\infty$, $n_o = N/V$ fixed) of the averages in (I.13).

$\tilde{\tilde{G}}(\vec{r},t)$ is known as the Van Hove self correlation function and expresses for a system in total equilibrium the probability of finding the tagged particle at time t at the position $\vec{\rho}+\vec{r}$, when it was initially (t=o) at the position $\vec{\rho}$. Due to translational and rotational invariance of the system, this probability depends only on $|\vec{r}|$ and t. Notice that $\tilde{\tilde{G}}(\vec{r},t)$ is independent of the initial density disturbance $W(\vec{r})$ and so we conclude from (I.12) that the choice (I.11) for the initial ensemble leads essentially to a linear self diffusion theory, i.e. $P(\vec{r},t)$ is linearly dependent on its initial value $W(\vec{r})$.. Furthermore, as can be seen from (I.12), $\tilde{\tilde{G}}(\vec{r},t)$ may be considered as the Green's function, which determines completely the decay of any initial density disturbance $W(\vec{r})$. Therefore we will study the function $\tilde{\tilde{G}}(\vec{r},t)$ rather than $P(\vec{r},t)$.

It will be convenient to consider spatial Fourier transforms of functions of $\vec{r}$, defined as

$$f(\vec{k}) \equiv \int_V d\vec{r}\ e^{-i\vec{k}.\vec{r}}\ \tilde{f}(\vec{r})\ . \qquad (I.14a)$$

Its inverse is given by

$$\tilde{f}(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} e^{i\vec{k}.\vec{r}} f(\vec{k}) , \tag{I.14b}$$

where $\vec{k}$ runs over the reciprocal lattice of V. For large volumes and smooth functions of $\vec{k}$ we may replace the sum $V^{-1} \sum_{\vec{k}} \ldots$ by the integral $(2\pi)^{-d} \int d\vec{k} \ldots$, where d is the dimensionality of the system. We also need the Laplace transform of functions of time defined as

$$f(z) = \int_0^\infty dt\ e^{-zt} \tilde{f}(t) . \tag{I.15}$$

The tildes in (I.14) and (I.15) will be omitted if no confusion can occur. In addition we define an innerproduct in the space of phase functions as

$$< f \mid g > \equiv < f^*(\Gamma)\ g(\Gamma) > , \tag{I.16}$$

where the left hand side is Dirac's notation of the innerproduct, the right hand side the canonical equilibrium average and the asterisk stands for complex conjugation.

For microscopic functions $f(\Gamma)$ not explicitly dependent on time we write shortly

$$S_t\ f(\Gamma) \equiv f(\Gamma(t)) \equiv f(t) .$$

The spatial Fourier transform of $\tilde{\tilde{G}}(\vec{r},t)$, known as the intermediate scattering function can now be expressed as

$$\tilde{G}(\vec{k},t) = < n(\vec{k}) \mid n(\vec{k},t) > = < e^{-i\vec{k}.\Delta\vec{r}_1(t)} > , \tag{I.17}$$

where $n(\vec{k}) \equiv \exp(-i\vec{k}.\vec{r}_1)$ is the Fourier transform of the microscopic tagged particle density $\delta(\vec{r}_1-\vec{r})$.

The Fourier-Laplace transform of $\tilde{\tilde{G}}(\vec{r},t)$, finally, can be expressed as

$$. \quad G(\vec{k},z) = < n(\vec{k}) \mid \frac{1}{z-L} \mid n(\vec{k}) > . \qquad \text{(I.18)}$$

Because $\tilde{\tilde{G}}(\vec{r},t)$, $\tilde{G}(\vec{k},t)$ and $G(\vec{k},z)$ are only dependent on the lengths r and k , we frequently omit the vector symbols.

b. Fick's Law

In this section we give a brief outline of the phenomenological macroscopic linear diffusion theory. In this theory the self diffusion process is basically described by Fick's law (Brush 1972; Hirschfelder 1967; Chapman 1960; De Groot 1962).
The ideas used in the phenomenological derivation of Fick's law are similar to those occurring in other macroscopic linear transport theories such as the Navier Stokes description of a general fluid near equilibrium (De Groot 1962). One associates with the probability density $P(\vec{r},t)$ defined in (I.9), a probability current density $\vec{J}(\vec{r},t)$, defined equivalently to (I.9) as the non-equilibrium average of the microscopic current density of tagged particles $\vec{v}_1\delta(\vec{r}-\vec{r}_1)$.
Due to the conservation of probability density, there is an exact relation between P and $\vec{J}$

$$\frac{\partial}{\partial t} P(\vec{r},t) = -\vec{\nabla} \cdot \vec{J}(\vec{r},t) , \tag{I.19}$$

which is the continuity equation and follows directly from Liouville's equation (I.10). In order to derive the phenomenological diffusion equation one supplements the conservation equation with the so called linear constitutive relations of irreversible thermodynamics, stating that $\vec{J}(\vec{r},t)$ is proportional to the gradient of the density $P(\vec{r},t)$ at the same position $\vec{r}$ and time t

$$\vec{J}(\vec{r},t) \simeq -D\, \vec{\nabla} P(\vec{r},t) . \tag{I.20}$$

This constitutive relation is known as Fick's law. The relation is expected to be approximately valid for small gradients; i.e. $P(\vec{r},t)$ varies slowly over distances of microscopic size, and for times large compared to microscopic time scales. The proportionality constant D is assumed to be positive and is called the self diffusion coefficient.

Generally in irreversible thermodynamics proportionality constants in constitutive relations depend on the *local* density and *local* temperature of the system and are, therefore, functions of position and time. Since we have restricted ourselves to the linear case, i.e. to situations near *total* equilibrium as described in section *a*, the coefficient D depends on the equilibrium density and temperature only. Combination of both relations for P and $\vec{J}$ yields a closed equation for $P(\vec{r},t)$ known as the linear (self) diffusion equation, or Fick's law

$$\cdot \quad \frac{\partial}{\partial t} P(\vec{r},t) \simeq D \nabla^2 P(\vec{r},t) \ . \tag{I.21}$$

Since we are dealing with linear deviations from total equilibrium, equation (I.12) implies relation (I.21) for $\tilde{\tilde{G}}(\vec{r},t)$ too. Therefore Fick's law may be stated in the following equivalent forms

$$\cdot \quad \frac{\partial}{\partial t} \tilde{\tilde{G}}(\vec{r},t) \simeq D \nabla^2 \tilde{\tilde{G}}(\vec{r},t) \tag{I.22}$$

$$\cdot \quad \frac{\partial}{\partial t} \tilde{G}(\vec{k},t) \simeq - Dk^2 \tilde{G}(\vec{k},t) \tag{I.23}$$

$$\cdot \quad G(\vec{k},z) \simeq \frac{1}{z+Dk^2} \ . \tag{I.24}$$

In the last line we used the fact that $\tilde{G}(\vec{k},t=o) = 1$, which follows from the initial condition $\tilde{\tilde{G}}(\vec{r},t=o) = \delta(\vec{r})$.
The solutions of (I.22) and (I.23) are

$$\cdot \quad \tilde{G}(\vec{k},t) \simeq \exp(-Dk^2 t) \tag{I.25}$$

$$\cdot \quad \tilde{\tilde{G}}(\vec{r},t) \simeq (4\pi Dt)^{-d/2} \exp(-r^2/(4Dt)) \ , \tag{I.26}$$

where d is the dimensionality of the system.
These relations (I.22-26) are assumed to be approximately valid if distances are large compared to microscopic lengths, wave vectors

small compared to inverse microscopic lengths, times large compared to microscopic times and frequencies small compared to inverse microscopic times.

An important part of our study will be the verification and extension of such phenomenological laws on the basis of more fundamental theories.
Let us therefore discuss these points in somewhat more detail and focus our attention to the relation (I.23) for $\tilde{G}(\vec{k},t)$, which is assumed to be approximately valid for t much larger than microscopic times and k much smaller than inverse microscopic lengths. A direct method to verify such a prediction is by defining on the basis of a microscopic theory a quantity D(k,t) such that

$$\cdot \quad \frac{\partial}{\partial t}\tilde{G}(k,t) \equiv - k^2 D(k,t)\, \tilde{G}(k,t) \tag{I.27}$$

is an exact relation. Since this is a definition equation for D(k,t) we have

$$\cdot \quad D(k,t) = - \frac{1}{k^2}\frac{\partial}{\partial t} \log \tilde{G}(k,t) \, , \tag{I.28}$$

Substitution of relation (I.17) for $\tilde{G}(k,t)$ yields an expression for D(k,t) in terms of averages of microscopic quantities.
Then, one can study the function D(k,t) for small k values and large times and verify if the function $\lim_{k\to o} D(k,t)$ has indeed a limiting value for $t\to\infty$, which is then, by definition, the diffusion coefficient D .
In the next chapters we study the function D(o,t) from kinetic theory and mode coupling theory. The result will be that for three dimensional systems the limit $\lim_{t\to\infty} D(o,t)$ exists, while for two dimensional systems D(o,t) tends to infinity as $t\to\infty$. Therefore, Fick's law is valid in three dimensional systems and invalid in two dimensions.

A next important part of our study deals with the following questions, which can be posed for three dimensional systems at least. What are the next order corrections to Fick's law? Or, in what sense is Fick's law a first order approximation to $\tilde{G}(k,t)$ in a systematic theory?
An answer to the first question is suggested in phenomenological transport theory (Hirschfelder 1967) stating that the relation (I.20) can be extended to

$$\vec{J}\,(\vec{r},t) \simeq - D\,\vec{\nabla}\,P(\vec{r},t) - D^{(2)}\,\vec{\nabla}\,\nabla^2\,P(\vec{r},t)\ \ldots\,. \qquad \text{(I.29)}$$

That means: higher derivatives of the density P have to be taken into account, which introduces new proportionality constants, such as $D^{(2)}$...
The constant $D^{(2)}$ is called the super Burnett self diffusion coefficient.
Due to symmetry properties of the fluid, odd powers of the gradients are absent in the relation above. In irreversible thermodynamics this property is known as Curie's law (De Groot 1962).
Relation (I.29) yields for $\tilde{\tilde{G}}(r,t)$ and $\tilde{G}(k,t)$ the generalized diffusion equations

$$\frac{\partial}{\partial t}\,\tilde{\tilde{G}}(r,t) \simeq D\,\nabla^2\,\tilde{\tilde{G}}(r,t) + D^{(2)}\,\nabla^2\,\nabla^2\,\tilde{\tilde{G}}(r,t) + \ldots \qquad \text{(I.30)}$$

$$\frac{\partial}{\partial t}\,\tilde{G}(k,t) \simeq - k^2\,(\,D - k^2\,D^{(2)} + \ldots\,)\,\tilde{G}(k,t)\,. \qquad \text{(I.31)}$$

Again we discuss in the next chapters the verification of these generalized diffusion equations from kinetic theory and mode coupling theory. The method will be the following.
The quantity $D(k,t)$ defined in (I.28) will be expanded in powers of k at fixed values of t , yielding an exact equation of the form

$$\frac{\partial}{\partial t}\,\tilde{G}(k,t) = - k^2\,(\,D^{(o)}(t) - k^2\,D^{(2)}(t) + \ldots\,)\,\tilde{G}(k,t)\,.\text{(I.32)}$$

We refer to $D^{(o)}(t)$ as the time dependent diffusion coefficient and it is in fact equal to the function $D(o,t)$, discussed above. The quantity $D^{(2)}(t)$ is referred to as the time dependent super Burnett coefficient. One would expect that the quantities $D^{(o)}(t)$ and $D^{(2)}(t)$ approach constants for large values of t . If calculation of the microscopic formula would confirm this expectation, one would have verified the phenomenological equation (I.31). Explicit calculations on $D^{(o)}(t)$ performed in chapter III for three dimensional systems predict that $\lim_{t\to\infty} D^{(o)}(t)$ exists indeed, as already mentioned above. However, we will see in chapter III that $D^{(2)}(t)$ *diverges* as $t\to\infty$. So the phenomenological super Burnett coefficient introduced in equation (I.29) does *not* exist and we conclude that introducing higher order diffusion coefficients in equation (I.29) is not a meaningful way to extend Fick's law for three dimensional systems.

We will extend Fick's law in a rather different way, which was inspired by the work of Zwanzig (Zwanzig 1964). He discussed the following problem: In what limiting sense are the phenomenological Fick's law predictions (I.24-26) exact relations for the functions $\tilde{\tilde{G}}(r,t)$, $\tilde{G}(k,t)$ and $G(k,z)$? To that aim he introduces the concept of hydrodynamic limit, which will be considered now.

We illustrate this concept by means of Einstein's displacement formula, stating that the mean square displacement of the tagged particle in x direction, is proportional to t for large times, i.e. $\langle (\Delta x_1(t))^2 \rangle \simeq 2Dt$. In fact this relation is a consequence of Fick's law as will be seen in the next section. Einstein's formula implies that, for large times, the displacement measured in units $\sqrt{Dt}$ is a dimensionless quantity of order 1 , namely $\langle (\Delta x_1(t)/\sqrt{Dt})^2 \rangle \simeq 2$.

This observation suggests to measure typical distances in the diffusion problem in units $\sqrt{Dt}$, and one expects these scaled lengths to be of order 1 for large times. Therefore, for large times, it is more relevant to study the probability density $P(\vec{r},t)$ and the Green's function $\tilde{\tilde{G}}(r,t)$ as functions of the scaled distance $\rho = r/\sqrt{Dt}$ and of the time t , where ρ is considered to be of order 1 and t is considered to be large. Therefore, for fixed values of ρ , $1/t$ may be considered as a small ordering parameter.

If for a function of length and time, the limit $1/t \to o$ is taken at fixed values of the scaled length ρ , this limit is referred to as the hydrodynamic limit.

The expectation, as expressed by Zwanzig, is that Fick's law may be true exactly in this hydrodynamic limit.

Let us apply these ideas on the functions $\tilde{\tilde{G}}(r,t)$, $\tilde{G}(k,t)$ and $G(k,z)$. We consider $\tilde{\tilde{G}}(r,t)$ as a function of ρ and t . For finite values of ρ and large t one sees from (I.26) that $\tilde{\tilde{G}}(\rho\sqrt{Dt},t) \simeq (4\pi Dt)^{-d/2} \exp(-\rho^2/4)$. The exact function $\tilde{\tilde{G}}(r,t)$ is said to satisfy Fick's law if

$$\lim_{\substack{t\to\infty \\ \rho \text{ fixed}}} (4\pi Dt)^{d/2}\, \tilde{\tilde{G}}(\rho\sqrt{Dt},t) = \exp(-\rho^2/4) \ . \tag{I.33}$$

Next we consider the function $\tilde{G}(k,t)$ in the hydrodynamic limit. Since $\tilde{G}(k,t)$ is the Fourier transform of $\tilde{\tilde{G}}(r,t)$ we study this function, for large t , as function of dimensionless scaled wave numer $\kappa = k\sqrt{Dt}$, where $1/t$ is considered as the ordering parameter. Inversely we may consider $\tilde{G}(k,t)$ as a function of a dimensionless scaled time τ ($\tau = Dk^2t$) , while k is used as the small ordering parameter. From (I.25) follows then that $\tilde{G}(k,\tau/Dk^2) \simeq \exp(-\tau)$ for finite values of τ and small values of k .

Now, $\tilde{G}(k,t)$ satisfies Fick's law, if

$$\lim_{\substack{k\to o \\ \tau \text{ fixed}}} \tilde{G}(k,\tau/Dk^2) = \exp(-\tau) \ . \tag{I.34}$$

Since $G(k,z)$ is the Laplace transform of $\tilde{G}(k,t)$, we measure the frequency in units Dk^2 ($z=\zeta Dk^2$) and study the function $G(k,z)$ as a function of ζ (finite complex), while k is used as the ordering parameter. For finite ζ and k small Fick's law predicts $Dk^2 G(k,\zeta Dk^2) \simeq (\zeta+1)^{-1}$. Hence, G(k,z) statisfies Fick's law, if

$$\lim_{\substack{k\to o \\ \mathrm{Re}\zeta > o}} Dk^2\, G(k,\zeta Dk^2) = \frac{1}{\zeta+1} \;. \tag{I.35}$$

In this relation we excluded $\mathrm{Re}\zeta \leqslant o$, since G(k,z) is only defined for values of z with $\mathrm{Re}z > o$.(It may of course be continued analytically into $\mathrm{Re}z \leqslant o$).

We mention the following points concerning the relations (I.33-35):

- the advantage of stating Fick's law in this rigorous form will be, that these predictions can be verified from a more fundamental theory;
- the ansatz that $\tilde{\tilde{G}}(r,t)$, $\tilde{G}(k,t)$ and G(k,z) are essentially functions of a scaled quantity of order 1 and a small ordering parameter, is very helpful in extending Fick's law predictions beyond its lowest order term;
  this idea will be applied in chapter V, where the ordering parameters are used as expansion parameters;
  such extensions avoid the difficulties, which arise in introducing higher order diffusion coefficients in the constitutive relation (I.20);
- the relations (I.33-35) are not trivially equivalent;
  the non-trivial point is the interchanging of limits and integrals, which occur if one expresses one of the functions $\tilde{\tilde{G}}(r,t)$, $\tilde{G}(k,t)$, G(k,z) into another one;
- as mentioned above, it is expected that these relations are not valid for two dimensional systems;
  we return in chapter IV to the diffusion problem in two dimensions.

c. Moments of displacement and related quantities

Other quantities of interest in the diffusion problem are the moments of displacement of the tagged particle, $M^{(n)}(t)$, generally defined by

$$M^{(n)}(t) = \langle (\Delta x_1(t))^n \rangle \qquad (n=0,2,4,\ldots) \qquad (I.36)$$

where $\Delta x_1(t) = x_1(t)-x_1(o)$ is the x component of the displacement vector $\Delta\vec{r}_1(t)$. From symmetry properties of the ensemble average one easily sees that all the odd moments (n=1,3,5...) vanish.
The moments $M^{(n)}(t)$ occur in the expansion of $\widetilde{G}(k,t)$ in powers of k , as can be seen from eq. (I.17)

$$\widetilde{G}(k,t) = \sum_{n=o}^{\infty} \frac{(-k^2)^n}{(2n)!} M^{(2n)}(t) \qquad (I.37)$$

and therefore one has for n=0,1,2,...

$$M^{(2n)}(t) = (-)^n \frac{(2n)!}{n!} \lim_{k\to o} \left\{\frac{\partial}{\partial k^2}\right\}^n \widetilde{G}(k,t) \qquad (I.38a)$$

$$= \frac{2\,\pi^{(d-1)/2}\,\Gamma(n+\frac{1}{2})}{\Gamma(n+d/2)} \int_o^{\infty} dr\; r^{2n+d-1}\, \approx{G}(r,t) \;, \qquad (I.38b)$$

where d is the dimensionality of the system and $\Gamma(x)$ denotes the Γ function.
Notice that, if $\widetilde{G}(k,t)$ is (approximately) described by Fick's law (I.25) we may expect for the moments of displacement, if t is large

$$M^{(2n)}(t) \simeq \frac{(2n)!}{n!} (Dt)^n \;. \qquad (I.39)$$

This expression contains Einstein's displacement formula for n=1 .

We also will study the cumulants $M_c^{(n)}(t)$ (n=2,4,6,...) of the moments of displacement $M^{(n)}(t)$, defined by the series expansion

$$\log \tilde{G}(k,t) \equiv \sum_{n=1}^{\infty} \frac{(-k^2)^n}{(2n)!} M_c^{(2n)}(t) \ . \tag{I.40}$$

Therefore one has for n=1,2,...

$$M_c^{(2n)}(t) = (-)^n \frac{(2n)!}{n!} \lim_{k \to o} \left\{\frac{\partial}{\partial k^2}\right\}^n \log \tilde{G}(k,t) \ . \tag{I.41}$$

The cumulants and moments are related by recursion relations given in the literature (Kubo 1962). The first two of these are

$$M_c^{(2)}(t) = M^{(2)}(t) \tag{I.42}$$

$$M_c^{(4)}(t) = M^{(4)}(t) - 3(M^{(2)}(t))^2 \ . \tag{I.43}$$

There exists a simple relationship between the cumulants and the time dependent diffusion coefficients $D^{(o)}(t)$, $D^{(2)}(t)$, ... defined in (I.32).
One easily sees from (I.32) and (I.40) that

$$D^{(2n)}(t) = \frac{1}{(2n+2)!} \frac{\partial}{\partial t} M_c^{(2n+2)}(t) \ . \qquad (n=0,1,\ldots) \tag{I.44}$$

As was already discussed in the previous section formal expressions for the time dependent diffusion coefficients can be used to verify phenomenological transport equations of the form (I.30,31). We derive, therefore, expressions for $D^{(o)}(t)$ and $D^{(2)}(t)$ in terms of averages of microscopic quantities.
For $D^{(o)}(t)$ we see from (I.44) that

$$D^{(o)}(t) = \tfrac{1}{2} \frac{\partial}{\partial t} < (\Delta x_1(t))^2 > \; .$$

By writing $\Delta x_1(t) = \int_o^t dt' \; v_{1x}(t')$ and employing symmetry properties of the streaming operator and the ensemble average, one obtains

$$D^{(o)}(t) = \int_o^t dt' < v_{1x} \; v_{1x}(t') > . \qquad (I.45)$$

The same procedure can be applied straightforwardly to $D^{(2)}(t)$ yielding

$$D^{(2)}(t) = E(t) - E_1(t) - E_2(t) - E_3(t) \qquad (I.46)$$

$$E(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 < v_{1x} \; v_{1x}(t_1) \; v_{1x}(t_2) \; v_{1x}(t_3) > \qquad (I.47)$$

$$E_1(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 < v_{1x} \; v_{1x}(t_1) > < v_{1x}(t_2) \; v_{1x}(t_3) > \qquad (I.48)$$

$$E_2(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 < v_{1x} \; v_{1x}(t_2) > < v_{1x}(t_1) \; v_{1x}(t_3) > \qquad (I.49)$$

$$E_3(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 < v_{1x} \; v_{1x}(t_3) > < v_{1x}(t_1) \; v_{1x}(t_2) > \qquad (I.50)$$

So $D^{(2)}(t)$ is expressed as an ordered time integral over the cumulant of the four point velocity correlation function. An analogous procedure has been used by McLennan (McLennan 1973). These expressions are convenient to study $D^{(o)}(t)$ and $D^{(2)}(t)$ in the framework of kinetic theory. In chapter III and IV we employ kinetic theory to calculate the correlation functions occurring in the expressions above for $D^{(o)}(t)$ and $D^{(2)}(t)$, both in two and three dimensions. These functions are calculated since we want to study the phenomenological transport equations (I,30,31), as was discussed in the previous section.

The calculations are performed with still another purpose. We start with the three dimensional case first.

The expressions given in chapter III for $D^{(o)}(t)$ and $D^{(2)}(t)$ are derived from first principles, but restricted to low densities and hard core interactions. On the other hand there is mode coupling theory (discussed in chapter V for d=3), which is able to predict the long time behaviour of $D^{(o)}(t)$ and $D^{(2)}(t)$. This theory is *not* restricted to low densities and hard sphere interactions. However the mode coupling theory is a phenomenological theory and therefore it is not a priori clear that $D^{(o)}(t)$ and $D^{(2)}(t)$ are predicted correctly. Therefore we compare the results from both theories in their common region of validity (i.e. low densities, hard core interactions, long times). This serves as a test for mode coupling theory. The results agree as we will see from chapter III and V, where many consequences of the mode coupling theory are further explored. This fact gives some support to the validity of the mode coupling theory for liquid densities, since in the phenomenological derivation (Kawasaki 1966; Kadanoff 1968; Ernst 1970), of the mode coupling formula no restrictions are imposed on the density.
Recently Wood (Wood 1974) performed computer simulation experiments for hard sphere systems at these densities. He was able to measure "experimentally" the functions $D^{(o)}(t)$ and $D^{(2)}(t)$ in great detail.
As further support for the mode coupling theory we want to mention here already that also for liquid densities the agreement between theory and experiment is very good for $D^{(o)}(t)$ (or rather its time derivative, which is the velocity correlation function), as Wood has shown (Wood 1974) by analyzing the effects of the finite size of the system, which are quite large in the three dimensional case. For $D^{(2)}(t)$ the agreement between theory and experiment is not quite impressive. As Wood discussed this could be due to finite size effects, an analysis of which must still be carried out for this case.

Next we consider the two dimensional case.
It is known already from computer simulation experiments (Alder 1970), from kinetic theory of hard disks (Pomeau 1971; Dorfman 1970, 1972)

and from mode coupling theory (Ernst 1970; Kawasaki 1970a) that the velocity correlation function in two dimensional systems behaves as $1/t$ for large times. Therefore $D^{(o)}(t)$ is proportional to $\log t$ and Fick's law is invalid, as was mentioned in the previous section; the super Burnett coefficient $D^{(2)}(t)$ diverges even stronger as will be shown in chapter IV.

Wood (Wood 1974) measured "experimentally" the functions $D^{(o)}(t)$ and $D^{(2)}(t)$ for two dimensional hard disk systems too. Generally, computer simulation experiments are easier to perform in two dimensions, where finite size effects are considerably smaller.

Therefore we calculate in chapter IV the functions $D^{(o)}(t)$ and $D^{(2)}(t)$ from kinetic theory of hard disks at low densities. We compare our predictions (especially for $D^{(2)}(t)$) with a few computer results at the same (*low*) density and the agreement turns out to be much better for the two dimensional system, than for the three dimensional case.

In the context of this dissertation a logical counterpart for the kinetic theory calculations of $D^{(o)}(t)$ and $D^{(2)}(t)$ for two dimensional systems in chapter IV would be a calculation of these quantities on the basis of the mode coupling theory for general densities, for which more extensive computer results are available than for low densities. A preliminary investigation of $D^{(o)}(t)$ and $D^{(2)}(t)$ on the basis of the mode coupling theory did indeed give a first approximation, which agrees very well with the computer calculations at liquid densities. Unfortunately there is a number of unresolved problems concerning the magnitude of the higher order approximations. For this reason we will not consider the two dimensional hard disk system at higher densities.

d. Projection Operator Techniques

During the last 15 years methods have been developed (Zwanzig 1961; Mori 1962, 1965) to derive formally exact linear transport equations involving non-local and non-instantaneous transport kernels, starting from the microscopic equations of motion and taking only linear deviations from equilibrium into account.
Such exact equations are useful as a tool to derive from first principles the macroscopic linear transport equations (such as Fick's law) and to study under which conditions such phenomenological equations may be valid. Furthermore this method yields expressions for the transport coefficients in terms of time integrals over equilibrium time correlation functions, known as Green-Kubo formulae. The method used to derive such exact equations is known as the projection operator technique and will be applied here to the case of self diffusion.

The starting point is the equation of motion for microscopic density functions. Here we only have the equation of motion for the microscopic tagged particle density $\frac{\partial}{\partial t} n(\vec{k},t) = L\, n(\vec{k},t)$. To obtain the macroscopic density $\tilde{G}(k,t)$ from the microscopic function $n(\vec{k},t)$, one observes from (I.17) that one does not need $| n(\vec{k},t) >$ in full detail but only its projection on $| n(\vec{k}) >$.
Therefore one defines the operator P in the space of phase functions as

$$P = \sum_{\vec{k}} | n(\vec{k}) > < n(\vec{k}) | \, . \tag{I.51}$$

This is a projection operator with the property $P^2 = P$ due to the fact that the functions $n(\vec{k})$ are normalized such that $< n(\vec{k}) | n(\vec{k}) > = 1$ and they form an orthonormal set for values of $\vec{k}$ in the reciprocal lattice of the volume V . With this pro'ection operator one may rewrite (I.17) as

$$\tilde{G}(k,t) = \langle n(\vec{k}) \mid P \mid n(\vec{k},t) \rangle .$$

The idea of the projection operator method is that one derives from the equation of motion for the full microscopic density $\mid n(\vec{k},t) \rangle$ an equation of motion for the relevant part $P \mid n(\vec{k},t) \rangle$. This can be done by applying the projection operators P and $1-P = P_\perp$ to the full equation of motion of $\mid n(\vec{k},t) \rangle$ yielding two coupled equations for $P \mid n(\vec{k},t) \rangle$ and $P_\perp \mid n(\vec{k},t) \rangle$. By changing to the Laplace transforms, both equations can be solved algebraically by eliminating the Laplace transform of $P_\perp \mid n(\vec{k},t) \rangle$, yielding a closed equation of motion for the Laplace transform of $P \mid n(\vec{k},t) \rangle$.
Here we follow a slightly different presentation, which is more convenient for our purpose.
We start from the following operator identity

$$\frac{1}{z-L} = \frac{1}{z-\hat{L}} + \frac{1}{z-\hat{L}} \{ PLP_\perp + P_\perp LP \} \frac{1}{z-L} . \tag{I.52}$$

Here we have defined $\hat{L}$ as the orthogonal part of the Liouville operator L

$$\hat{L} = P_\perp L P_\perp \tag{I.53}$$

and we have used the relation

$$PLP = o , \tag{I.54}$$

which follows from the anti-hermitean property of L.
Further useful properties are

$$P \frac{1}{z-\hat{L}} P = \frac{1}{z} P \; ; \; P_\perp \frac{1}{z-\hat{L}} P = o .$$

Applying the identity (I.52) to the expression (I.18) for G(k,z) yields directly

$$G(k,z) = \frac{1}{z} + \frac{1}{z} < n(\vec{k}) \mid LP_{\perp} \frac{1}{z-L} \mid n(\vec{k}) > .$$

The identity (I.52) can be applied once more, yielding

$$G(k,z) = \frac{1}{z} + \frac{1}{z} < n(\vec{k}) \mid LP_{\perp} \frac{1}{z-\hat{L}} P_{\perp} LP \frac{1}{z-L} \mid n(\vec{k}) > .$$

The Liouville operator acting on the density is equal to

$$L \mid n(\vec{k}) > = - ik \mid j(\vec{k}) > , \tag{I.55}$$

where $j(\vec{k})$ is the microscopic tagged particle current density defined as a scalar quantity

$$j(\vec{k}) = \vec{v}_1 . \hat{k} \exp(-i\vec{k}.\vec{r}_1) , \tag{I.56}$$

where $\hat{k} = \vec{k}/k$ is a unit vector in the $\vec{k}$ direction. With the help of (I.55) one finally arrives at an exact result for $G(k,z)$

$$G(k,z) = \frac{1}{z+k^2 U(k,z)} . \tag{I.57}$$

This has the form of a generalized transport equation (compare (I.24)) with a wave number and frequency dependent diffusion coefficient $U(k,z)$ given by

$$U(k,z) = < j(\vec{k}) \mid \frac{1}{z-\hat{L}} \mid j(\vec{k}) > . \tag{I.58}$$

Its inverse Laplace transform is

$$\tilde{U}(k,t) = < j(\vec{k}) \mid \exp(t\hat{L}) \mid j(\vec{k}) > . \tag{I.59}$$

The generalized diffusion equation (I.57) yields in $(\vec{k},t)$-language

$$\frac{\partial}{\partial t}\tilde{G}(\vec{k},t) = - k^2 \int_o^t dt' \; \tilde{U}(\vec{k},t') \; \tilde{G}(\vec{k},t-t') \tag{I.60}$$

and in $(\vec{r},t)$-language

$$\frac{\partial}{\partial t}\tilde{\tilde{G}}(\vec{r},t) = \nabla^2 \int_o^t dt' \int d\vec{r}' \; \tilde{\tilde{U}}(\vec{r}',t') \; \tilde{\tilde{G}}(\vec{r}-\vec{r}',t-t') \; . \tag{I.61}$$

The exact relation (I.60) has the form of a diffusion equation with a wave vector dependent memory kernel and should be compared with (I.23). The exact relation (I.61) has the form of a non-local non-instantaneous type of diffusion equation and should be compared with (I.22).

The wave number dependent projected current correlation function $\tilde{U}(k,t)$ is related to the ordinary current correlation function $\tilde{C}(k,t)$, defined as

$$\tilde{C}(k,t) = < j(\vec{k}) \mid \exp(tL) \mid j(\vec{k}) > = < j^{*}(k)\, j(\vec{k},t) > \tag{I.62}$$

with a Laplace transform

$$C(k,z) = < j(\vec{k}) \mid \frac{1}{z-L} \mid j(\vec{k}) > . \tag{I.63}$$

The relation mentioned here can most easily be found in Laplace language by applying the operator identity (I.52), yielding

$$C(k,z) = \frac{zU(k,z)}{z+k^2U(k,z)} \; . \tag{I.64}$$

Let us summarize some further properties of the functions $U(k,z)$ and $C(k,z)$ valid for two and three dimensional systems. There exist trivial upper bounds on the functions $\tilde{U}(k,t)$ and $\tilde{C}(k,t)$ as follows from (I.59) and (I.62)

$$\mid \tilde{U}(k,t) \mid \leqslant \tilde{U}(k,t{=}o) = (\beta m)^{-1}$$

$$\cdot \quad |\ \tilde{C}(k,t)\ | \leqslant \tilde{C}(k,t=o) = (\beta m)^{-1} \tag{I.65}$$

valid for all values of k and t .
The Laplace transfroms $U(k,z)$ and $C(k,z)$ are, for any k , analytic functions of z , for all values of z with $Rez > o$. If $Rez > o$, the Laplace transforms are bounded by

$$\cdot \quad |\ U(k,z)\ | \leqslant (\beta m)^{-1}/Rez$$

$$\cdot \quad |\ C(k,z)\ | \leqslant (\beta m)^{-1}/Rez\ . \tag{I.66}$$

If $Rez \geqslant o$, the limits $k \to o$ of $U(k,z)$ and $C(k,z)$ are well defined and equal to

$$\cdot \quad \lim_{k \to o} U(k,z) = \int_o^\infty dt\ e^{-zt}\ \tilde{U}(o,t) = U(o,z)$$

$$\cdot \quad \lim_{k \to o} C(k,z) = \int_o^\infty dt\ e^{-zt}\ \tilde{C}(o,t) = C(o,z)\ .$$

Since the limits exist it is clear from (I.64) that $U(o,z) = C(o,z)$.
The function $\tilde{C}(k,t)$ converges for $k \to o$ to the velocity correlation function $< v_{1x}\ v_{1x}(t) >$, as can be seen from (I.62) and (I.56). We will write shortly $< v_{1x}\ v_{1x}(t) > = \tilde{C}(t)$.
We may conclude from these considerations that

$$\cdot \quad \lim_{k \to o} U(k,z) = \lim_{k \to o} C(k,z) = U(o,z) = C(o,z)$$

$$= C(z) = \int_o^\infty dt\ e^{-zt}\ < v_{1x}\ v_{1x}(t) > \tag{I.67}$$

$$\cdot \quad \lim_{k \to o} \tilde{U}(k,t) = \lim_{k \to o} \tilde{C}(k,t) = \tilde{U}(o,t) = \tilde{C}(o,t)$$

$$= \tilde{C}(t) = < v_{1x}\ v_{1x}(t) >\ , \tag{I.68}$$

where (I.67) is valid for $\mathrm{Re}\,z > 0$ only.
We note that very little can be said, in general, about the behaviour of $U(k,z)$ and $C(k,z)$ if z tends to zero at fixed values of k .

Next we study conditions under which the phenomenological predictions of Fick's law (I.33-35) can be obtained from the exact relation (I.57). From (I.35) it is clear that one has to assume something about the behaviour of $U(k,z)$ for small values of k and z . Zwanzig suggests (Zwanzig 1964) that it is reasonable to expect $U(k,z)$ to be bounded (for three dimensional systems) in the neighbourhood of $k=0$, $z=0$ and he uses that $U(k,z)$ is even continuous there.
The arguments deal with the fact that in the denominator of the expression (I.58) for $U(k,z)$ the operator $\hat{L} = P_{\perp} L P_{\perp}$ occurs. P is the projection operator on the functions $n(\vec{k})$. For values of $k \to 0$, $n(\vec{k})$ approaches an eigenfunction of L (the unit function) with eigenvalue zero. The operator $P_{\perp}$ projects orthogonal to these functions and therefore it may be plausible that $U(k,z)$ (in three dimensional systems) is bounded or even continuous near $k=0$, $z=0$. The plausibility of this argument is of course rather weak, since it leads to incorrect results in two dimensional systems, where it is known that the $\lim_{z \to 0} U(0,z)$ does not exist, as was discussed in the previous section.
The above arguments do not apply to $C(k,z)$ since the expression (I.63) contains the full Liouville operator in the denominator. The behaviour of $C(k,z)$ and $U(k,z)$ may be quite different near $k=0$, $z=0$.
Keeping this in mind, one could impose the following conditions on $U(k,z)$:

(i) $U(k,z)$ is a continuous function of k and z with a well defined value at $k=0$, $z=0$, which is by definition the self diffusion coefficient D: $U(0,0) = D$, (I.69a)

(ii) $U(k,z)$ is uniformly bounded for all (real) values of $k \geqslant 0$ and complex values of z with $\mathrm{Re}\, z \geqslant 0$, (I.69b)

and one would have to show that (I.69) implies the predictions of Fick's law formulated in (I.33-35).

Requirement (i) implies the exact relation (I.35) for $G(k,z)$ as can be shown immediately from (I.57).

The requirements (i) and (ii) do not trivially imply the exact relations (I.34) and (I.33) for $\tilde{G}(k,t)$ and $\tilde{\tilde{G}}(r,t)$. The non-trivial point again is the interchanging of limits and integrals. Notice that, *if* the limits and integrals may be interchanged, these relations follow immediately.

One can indeed show that (i) and (ii) are sufficient to derive relation (I.34) for $\tilde{G}(k,t)$.

However it is not clear whether (i) and (ii) are sufficient conditions to prove (I.33) for $\tilde{\tilde{G}}(r,t)$.

Although a derivation of relation (I.33) for $\tilde{\tilde{G}}(r,t)$ from conditions (i) and (ii) (and possibly more) is still lacking we say that $U(k,z)$ satisfies Fick's law if the conditions (i) and (ii) for $U(k,z)$ are fulfilled.

We introduced this version of Fick's law, since it is helpful in chapter V, where we study mode coupling theory, which essentially deals with the function $U(k,z)$.

Before concluding this section we make a number of remarks concerning (I.69):

- requirement (i) implies the well known expression for the self diffusion coefficient

$$D = \int_0^\infty dt < v_{1x}\, v_{1x}(t) > \qquad \text{(I.70)}$$

  as can be seen from (I.67);
  this relation is consistent with relation (I.45) for $D^{(o)}(t)$ and the definition for the diffusion coefficient discussed in section *b*,

- $D = \lim_{t\to\infty} D^{(o)}(t)$;

- requirement (i) implies for $C(k,z)$

- $$\lim_{z\to o}\lim_{k\to o} C(k,z) = D \tag{I.71}$$
- $$\lim_{\substack{k\to o \\ \zeta \text{ fixed}}} C(k,\zeta Dk^2) = \frac{\zeta}{\zeta+1} D \; ; \tag{I.72}$$

  therefore $C(k,z)$ is not continuous in $k=o$, $z=o$;
  this point was discussed above;
- requirement (ii) is an extension of property (I.66), which implies that $U(k,z)$ is uniformly bounded for all values of k and all values of z with $\mathrm{Re}\,z \geqslant \epsilon$, where ϵ is positive; from requirement (i) follows only that $U(k,z)$ is bounded for *small* values of k and z ; the requirement (ii) excludes, for any value of k , the possibility of singularities on the imaginary axis, in complex z plane, where the function $U(k,z)$ is infinite.

CHAPTER II

Kinetic theory of hard spheres at low densities

a. Binary Collision Expansion

The first purpose of this dissertation concerns the verification of phenomenological transport equations like (I.20) and (I.29), from first principles. For that reason we want to calculate the long time behaviour of the functions $D^{(o)}(t)$ and $D^{(2)}(t)$ defined in (I.32).
The next purpose of such a calculation is the justification of phenomenological mode coupling theory and the comparison with results from computer simulation experiments. These points were discussed in chapter I .

The relative simplest and most well developed theory derived from the Liouville equation and capable of describing the long time behaviour of $D^{(o)}(t)$ and $D^{(2)}(t)$ is the kinetic theory of hard spheres at low densities.
In the last decennium the main interest of kinetic theory was to develop density expansions for transport coefficients, such as the self diffusion constant D . For a review see e.g. (Ernst 1969a).
Later on the low density version of kinetic theory was employed to calculate the velocity correlation function (which is the time derivative of $D^{(o)}(t)$) (Dorfman 1970, 1972; Pomeau 1971). In this chapter we extend this low density version, such that $D^{(2)}(t)$ can be calculated too. The actual calculations of $D^{(o)}(t)$ and $D^{(2)}(t)$ will be performed in chapter III (d=3) and chapter IV (d=2) .

Here a brief outline is given of the kinetic theory of hard spheres at low densities and it will be indicated how it can be derived starting from the binary collision expansion for the streaming operator S_t (Zwanzig 1963), defined in (I.4).

We use a diagrammatic method to study kinetic theory, which has in fact been used by many authors for deriving kinetic equations; see e.g. (Van Leeuwen 1965; Kawasaki 1965; Weijland 1967; Van Beijeren 1974). We will review and slightly modify these diagrammatic representations.

A convenient description of kinetic theory can be given in terms of the kinetic (self) propagator for the tagged particle $\overline{\Gamma}^s_{\vec{k}}(1,t)$, which is a wave number dependent one particle operator acting on functions of $\vec{v}_1$ only and defined by

$$< f(\vec{v}_1)\, e^{i\vec{k}.\vec{r}_1}\, S_t\, g(\vec{v}_1)\, e^{-i\vec{k}.\vec{r}_1} > \equiv < f(\vec{v}_1)\, \overline{\Gamma}^s_{\vec{k}}(1,t) g(\vec{v}_1) >_1 . \tag{II.1}$$

Here f and g are arbitrary functions of $\vec{v}_1$; the left hand side contains the N body streaming operator and the canonical ensemble average; the right hand side is expressed as a one particle average, defined for any subscript i as

$$< f(\vec{v}_i) >_i \equiv \int d\vec{v}_i\, \phi_o(v_i)\, f(\vec{v}_i) . \tag{II.2}$$

The normalized Maxwellian is given by

$$\phi_o(v) = \left(\frac{\beta m}{2\pi}\right)^{d/2} \exp(-\tfrac{1}{2}\beta m v^2) . \tag{II.3}$$

We note that the tagged particle streaming operator $\overline{\Gamma}^s_{\vec{k}}(1,t)$ still contains the full N body dynamics.

In addition we introduce the kinetic propagator for a fluid particle $\overline{\Gamma}_{\vec{k}}(i,t)$, which is a one particle operator acting on functions of $\vec{v}_i$ only, and is defined by

$$N^{-1} < \sum_{m=1}^{N} f(\vec{v}_m)\, e^{i\vec{k}.\vec{r}_m}\, S_t \sum_{j=1}^{N} g(\vec{v}_j)\, e^{-i\vec{k}.\vec{r}_j} > \equiv$$

$$< f(\vec{v}_i)\, \overline{\Gamma}_{\vec{k}}(i,t)\, g(\vec{v}_i) >_i \,, \tag{II.4}$$

where i may be any number except 1 (to avoid confusion with the tagged particle).

Strictly speaking the relations (II.1) and (II.4) are introduced for finite systems. The thermodynamic limit will be taken at the end of the calculations.

Note that $\overline{\Gamma}_{\vec{k}}(i,t)$ describes the joint correlation functions between any fluid particle at time t and any fluid particle at the initial time, while $\overline{\Gamma}^s_{\vec{k}}(1,t)$ describes the correlation functions of the tagged particle.

In particular the tagged particle current correlation function $\tilde{C}(\vec{k},t)$ defined in (I.62) can immediately be written as a one particle average

$$\tilde{C}(\vec{k},t) = < \vec{v}_1.\hat{k}\, \overline{\Gamma}^s_{\vec{k}}(1,t)\, \vec{v}_1.\hat{k} >_1 \,. \tag{II.5}$$

The k=o limit of this expression yields for the velocity correlation function

$$\tilde{C}(t) = < v_{1x}\, v_{1x}(t) > = < v_{1x}\, \overline{\Gamma}^s_o(1,t)\, v_{1x} >_1 \,. \tag{II.6}$$

In the remainder of this section we develop a kinetic theory for the special case of hard sphere systems, which leads to the diagrammatic representation for the propagators $\overline{\Gamma}_{\vec{k}}$ and $\overline{\Gamma}^s_{\vec{k}}$ as given in the next section.

The starting point is the binary collision expansion for the streaming operator S_t applied to the case of hard spheres.

For hard spheres the first problem is the non-existence of the operators Θ_a occurring in the Liouville operator (I.5). Because the operator S_t is well defined, also in hard sphere systems and generates the dynamics for all configurations, which are physically possible, one usually introduces a pseudo streaming operator by (Ernst 1969b)

$$S_t = \exp \{ t (\sum_i L_o(i) + \sum_a T(a)) \} . \tag{II.7}$$

S_t is called a *pseudo* streaming operator since it is also defined for overlapping configurations, where the centers of any number of hard spheres are inside the action sphere of any other particle.
The operators $L_o(i)$ are defined in (I.6). The binary collision operator $T(a)$, where a denotes a pair of particles (ij) , is given by

$$T(ij) = \sigma^{d-1} \int_{\vec{v}_{ij}\cdot\hat{\sigma}<o} d\hat{\sigma} \mid \vec{v}_{ij}\cdot\hat{\sigma} \mid \delta(\vec{r}_{ij}-\sigma\hat{\sigma}) \{ b_{\hat{\sigma}}(ij)-1 \} . \tag{II.8}$$

Here σ is the hard sphere diameter of the d dimensional spheres, $\hat{\sigma}$ a unit vector and the $\hat{\sigma}$ integration is an angular integration over the d dimensional unit sphere. The operator $b_{\hat{\sigma}}(ij)$, acting on phase functions, replaces the velocities $\vec{v}_i$ and $\vec{v}_j$ by their values after a collision of the particles i and j

$$b_{\hat{\sigma}}(ij)\, \vec{v}_i = \vec{v}_i - (\vec{v}_{ij}\cdot\hat{\sigma})\hat{\sigma}$$

$$b_{\hat{\sigma}}(ij)\, \vec{v}_j = \vec{v}_j + (\vec{v}_{ij}\cdot\hat{\sigma})\hat{\sigma} . \tag{II.9}$$

Due to the fact that in any collision between two particles the total energy, total momentum and the number of particles is conserved we have the following properties for the binary collision operator T(ij)

$$T(ij)\, f'(\Gamma) = o \tag{II.10a}$$

$$T(ij)\, (\vec{v}_i+\vec{v}_j)\, f'(\Gamma) = o \tag{II.10b}$$

$$T(ij)\, (v_i^2+v_j^2)\, f'(\Gamma) = o , \tag{II.10c}$$

where $f'(\Gamma)$ is any phase function independent of the phases of the particles i and j .

The binary collision expansion of the streaming operator expresses S_t as an infinite series involving products of free streaming operators S_t^o and binary collision operators $T(ij)$.
The free streaming operator generates the motion of particles in the absence of interactions, where it factorizes into

$$\cdot \quad S_t^o = \prod_{i=1}^{N} S_t^o(i) \; . \qquad \text{(II.11)}$$

Here $S_t^o(i)$ is the one particle free streaming operator, which formally can be written as

$$\cdot \quad S_t^o(i) = \exp \{ \, t \, L_o(i) \, \} \; , \qquad \text{(II.12)}$$

where $L_o(i)$ is given in (I.6). From (II.7), (II.11) and (II.12) it is easy to derive the relation

$$\cdot \quad S_t = S_t^o + (S^o \star \sum_{\alpha} T(\alpha) S \,)_t \; , \qquad \text{(II.13)}$$

where the asteriks denotes a convolution product in time defined as

$$\cdot \quad (f\star g)(t) \;\; \equiv \int_o^t dt' \; f(t') \; g(t-t') \; . \qquad \text{(II.14)}$$

Iteration of (II.13) yields the binary collision expansion for S_t

$$\cdot \quad S = S^o + S^o \star \sum_{\alpha} T(\alpha) \; S^o + S^o \star \sum_{\alpha} T(\alpha) \; S^o \star \sum_{\beta} T(\beta) \; S^o + \ldots$$

$$= S^o + \sum_{m=1}^{\infty} \sum_{\alpha_1} \; \ldots \sum_{\alpha_m} \; S^o \star T(\alpha_1) \; S^o \star \ldots \; T(\alpha_m) \; S^o \; , \qquad \text{(II.15)}$$

in which we have omitted the time dependence of the streaming operators.

Each term in the binary collision expansion is determined by an integer m (denoting the number of collision operators involved) and an ordered set of pairs of particles $(\alpha_1 , \dots , \alpha_m)$. It represents a dynamical process, the meaning of which can be obtained directly from the action of the binary collision operator $T(\alpha)$ and the free streaming operators.

Since two particles can never collide twice in the absence of interactions with other particles, we have the property $T(\alpha)\ S_t^o\ T(\alpha) = o$. Therefore the index pairs of subsequent T operators in the expansion (II.15) may taken to be different and then (II.15) reduces to the usual form given in the literature (Zwanzig 1963).

As the next step in developing a kinetic theory one substitutes the binary collision expansion (II.15) for S_t into the definition equations (II.1) and (II.4) for $\overline{\Gamma}^s_{\vec{k}}(1,t)$ and $\overline{\Gamma}_{\vec{k}}(i,t)$ respectively.

In the remainder of this section we consider the derivation of a diagrammatic representation for $\overline{\Gamma}^s_{\vec{k}}$ only. The derivation for $\overline{\Gamma}_{\vec{k}}$ goes along similar lines.

An explicit expression for $\overline{\Gamma}^s_{\vec{k}}(1,t)$ is obtained from the definition (II.1) specialized to the hard core system

$$\overline{\Gamma}^s_{\vec{k}}(1,t) = e^{i\vec{k}.\vec{r}_1} \frac{V}{Q_N(V)} \int \dots \int \left(\prod_{s=2}^{N} d\vec{r}_s\ d\vec{v}_s\ \phi_o(v_s) \right) W(\Gamma)\ [\mathrm{BCE}]\ e^{-i\vec{k}.\vec{r}_1} . \tag{II.16}$$

The integration over $\vec{r}_1$ yielding a factor V has been carried out since the integrand does not depend on $\vec{r}_1$ due to the translational invariance of the equilibrium state.

Here [BCE] represents the binary collision expansion (II.15) for the streaming operator S_t .

The overlap function $W(\Gamma) = W(\vec{r}_1 , \dots , \vec{r}_N)$ is zero for spatial configurations in which at least two particles overlap and it is one for all non-overlapping configurations. The configurational partition function $Q_N(V)$ is defined as

$$\cdot \quad Q_N(V) = \int d\vec{r}_1 \ \ldots \int d\vec{r}_N \ W(\Gamma) \ . \qquad \text{(II.17)}$$

The function $W(\Gamma)$ can be expanded in a series of Mayer functions (Uhlenbeck 1962)

$$\cdot \quad W(\Gamma) = \prod_{\alpha} (1+f_\alpha) = 1 + \sum_{\alpha} f_\alpha + \sum_{\alpha} \sum_{\beta \neq \alpha} f_\alpha f_\beta + \ldots , \qquad \text{(II.18)}$$

where the Mayer function $f_\alpha = f_{ij}$ equals zero if the particles i and j are outside each other and minus one otherwise.
This expansion together with the binary collision expansion (II.15) may be substituted into the relation (II.16) for $\overline{\Gamma}^S_{\vec{k}}$ and each term in the expansion for $\overline{\Gamma}^S_{\vec{k}}$ may be represented by a diagram.
Having obtained a diagrammatic representation of the propagator $\overline{\Gamma}^S_{\vec{k}}$ one can apply standard methods of many body theory to derive kinetic equations for the problems of interest.
Here we could apply this systematic theory to discuss the long time behaviour of the functions $D^{(o)}(t)$ and $D^{(2)}(t)$ for hard sphere systems, although the explicit calculations are rather complicated.
Therefore, to simplify the presentation, we restrict ourselves from now on to low densities.

First we state how the kinetic theory of hard spheres at low densities is obtained from the systematic theory

(i) Omit all statistical correlations in (II.16), i.e. replace the canonical distribution function of the hard sphere system by the distribution function of the ideal gas. Explicitly

$$\cdot \quad W(\Gamma) = 1 \qquad \text{(II.19a)}$$

$$Q_N(V) = V^N \; . \tag{II.19b}$$

(ii) Neglect the σ dependence of the δ function occurring in the expression (II.8) for the binary collision operator, i.e. write

$$T(ij) = \delta(\vec{r}_{ij})\, T_o(ij) \; , \tag{II.20}$$

where

$$T_o(ij) = \sigma^{d-1} \int_{\vec{v}_{ij}\cdot\hat{\sigma}<o} d\hat{\sigma}\, |\vec{v}_{ij}\cdot\hat{\sigma}|\, \{ b_{\hat{\sigma}}(ij) - 1 \} \; . \tag{II.21}$$

We refer to $T_o(ij)$ as the binary collision operator and note that it acts on the velocities of the particles i and j only.

Next we discuss these approximations and the validity of the resulting kinetic theory in more detail.
The study of kinetic theory has taught us already that virial expansions for transport coefficients do not exist. If one tries to find for a transport coefficient an expansion in powers of the density, almost all coefficients diverge. This is due to purely dynamical processes involved in the binary collision expansion (II.15), which contain persistent memory effects. These processes are described extensively in the literature (Cohen 1967), and we leave out the details here.
Furthermore it became clear that similar dynamical events were responsible for persistent correlations in the velocity correlation function (Dorfman 1970,1972,1974; Resibois 1974; Dufty 1974). They give contributions to time correlation functions (such as the velocity correlation function), which are slowly (i.e. non-exponentially) decaying functions of t/t_o . Here t_o is the mean free time between collisions and represents the relevant time scale in dynamical processes.
The systematic kinetic theory shows that the qualitative behaviour of

these *dynamical* processes (which arise from the binary collision expansion (II.15)) for *large* values of t/t_o , is unchanged, if *statistical* correlations are taken into account (which arise from the Mayer expansion (II.18)). Quantitatively, statistical correlations yield higher order density corrections to the contributions of purely dynamical processes.

We leave out a detailed proof of this statement but mention that it may be plausible from the following arguments.

The relevant scale to measure distances in dynamical processes is the mean free path l_o , which is of the order $l_o \sim \langle |v_1| \rangle t_o \sim 1/(n_o \sigma^{d-1})$. The relevant scale to measure distances in statistical correlations is the correlation length, which is of order σ . Therefore if one omits statistical correlations, one neglects contributions to the dynamical processes, which are of higher order in the density, since $\sigma / l_o \sim n_o \sigma^d$.

Next we consider the second approximation (II.20). The systematic theory shows that qualitatively the long time behaviour of dynamical processes is unchanged by this approximation, and quantitatively one neglects contributions of higher order in the density.

By comparing the Fourier transforms of $\delta(\vec{r}_{ij}-\sigma\hat{\sigma})$ (which occurs in the exact T operator (II.8)) and $\delta(\vec{r}_{ij})$ (which occurs in the approximation (II.20)) one observes, that the difference $\exp(-i\vec{k}.\sigma\hat{\sigma})-1$ is of higher order in the density for values of k , which are relevant in dynamical processes, i.e. $k \leqslant l_o^{-1}$.

In summary, one can show the following statements from the systematic theory:

- The approximate kinetic theory deduced from the approximations (II.19) and (II.20) predicts that certain dynamical processes give contributions to the velocity correlation function, which are slowly decaying functions of dimensionless time t/t_o . These processes give similar contributions to the time de endent super Burnett coefficient. If one collects all terms wi h the same asymptotic long time

behaviour, then our approximate kinetic theory predicts this behaviour correctly to lowest non-vanishing order in the density, with the following restriction.
The above statement does only hold for asymptotic corrections, which are larger than $O(t^{-1/2})$ *relative* to the dominant behaviour.
This point will be discussed further at the end of chapter III.

- For times of order t_o the approximate theory is equivalent with the linearized Boltzmann equation; i.e. it predicts the dominant short time behaviour in lowest order in the density.

Next we consider the resulting kinetic theory and sketch the derivation of a diagrammatic representation.
The approximations (II.19,20) yield for the kinetic self propagator $\overline{\Gamma}^s_{\vec{k}}$ the expression

$$\cdot \quad \overline{\Gamma}^s_{\vec{k}}(1,t) = e^{i\vec{k}.\vec{r}_1} V^{-N+1}$$

$$\int \cdots \int \prod_{s=2}^{N} \left(d\vec{r}_s \, d\vec{v}_s \, \phi_o(v_s) \right) [\mathrm{BCE}]' \, e^{-i\vec{k}.\vec{r}_1} , \qquad \text{(II.22)}$$

where the prime on [BCE] indicates that we have replaced all binary collision operators $T(a)$ occurring in the expansion (II.15) by the approximate expression (II.20). Each term in (II.15) yields one term in (II.22).
Next we study the non-vanishing contributions of each term in the binary collision expansion (II.15) to the propagator $\overline{\Gamma}^s_{\vec{k}}$ in (II.22).
To this aim the properties (II.10) are needed. From (II.10a), (II.20) and properties of the free streaming operator (II.12) it is easy to see that

$$\cdot \quad T_o(ij) \, S^o_t \, f'(\Gamma) = o ,$$

where $f'(\Gamma)$ is any phase function independent of the phases of particles i and j .
Since the operator $\overline{\Gamma}^{s}_{\vec{k}}$ acts on functions of $\vec{v}_1$ only, we have the following property for each non-vanishing term in the binary collision expansion (II.22):

- Reading a term in the BCE from the right to the left at least *one of the particle labels in each* $T_o(ij)$ *operator is equal to* 1 or equal to a particle label, which occurred already to the right. (II.23a)

The next property of non-vanishing terms in (II.22) is the hermitean conjugate property of (II.23a) and can be deduced directly from the hermiticity of $T_o(ij)$, with respect to the inner product (I.16):

- Reading a term in the BCE from the left to the right at least one of the particle labels in each $T_o(ij)$ operator is equal to 1 or equal to a particle label, which occurred already to the left. (II.23b)

Terms in the BCE, satisfying property (II.23a,b) can be distinguished according to the number of particles m (m=1,2,...,N) , whose labels are connected to one another through property (II.23a,b), and are called *connected* terms of m particles.
We perform in each connected m particle term the integrations over the spatial and velocity coordinates of the N-m particles, which are not connected to particle 1 , yielding a factor V^{N-m} , and we relabel the m connected particles with the labels 1,2,...,m in natural order as they occur from the left to the right in each term of the binary collision expansion.
There exists in the BCE (II.22) (N-1)!/(N-m)! identical terms, the sum of which is called the *weight* $W(N;C_m)$ of a connected m particle term C_m .

Hence we can write (II.22) as

$$\cdot \quad \overline{\Gamma}^{s}_{\vec{k}}(1,t) = \sum_{m=1}^{N} \sum_{\{C_m\}} W(N;C_m) \ , \tag{II.24a}$$

where

$$\cdot \quad W(N;C_m) = e^{i\vec{k}.\vec{r}_1} \ (N-1)!\,/(N-m)! \ \ V^{-m+1}$$

$$\int \cdots \int \Big(\prod_{s=2}^{m} d\vec{r}_s \ d\vec{v}_s \ \phi_o(v_s) \Big) \ C_m \ e^{-i\vec{k}.\vec{r}_1} \ . \tag{II.24b}$$

Here C_m represents a *connected* m particle term, in which the particles are labeled in *natural* order. The sum over $\{C_m\}$ in (II.24a) extends over all possible C_m terms with m particles.

In the thermodynamic limit ($V\to\infty, N\to\infty, N/V=n_o$ is fixed) we have

$$\cdot \quad \overline{\Gamma}^{s}_{\vec{k}}(1,t) = \sum_{m=1}^{\infty} \sum_{\{C_m\}} W(C_m) \ , \tag{II.25a}$$

where $W(C_m)$ is the thermodynamic limit of $W(N;C_m)$, and is given by

$$\cdot \quad W(C_m) = e^{i\vec{k}.\vec{r}_1} \ n_o^{m-1}$$

$$\int \cdots \int \Big(\prod_{s=2}^{m} d\vec{r}_s \ d\vec{v}_s \ \phi_o(v_s) \Big) \ C_m \ e^{-i\vec{k}.\vec{r}_1} \ , \tag{II.25b}$$

where the spatial integrations extend over infinite space.
As an illustration we consider the first two terms in (II.25a).
For m=1 we have

$$\cdot \quad W(C_1) = e^{i\vec{k}.\vec{r}_1} \ S^o_t(1) \ e^{-i\vec{k}.\vec{r}_1} = S^o_t(\vec{k},1) \ , \tag{II.26}$$

where $S_t^o(\vec{k},1)$ is the Fourier transform of the free streaming operator of particle 1

$$S_t^o(\vec{k},1) = \exp(-i\vec{k}.\vec{v}_1 t) . \qquad \text{(II.27)}$$

The next term with m=2 reads

$$W(C_2) = e^{i\vec{k}.\vec{r}_1} n_o \iint d\vec{r}_2\, d\vec{v}_2\, \phi_o(v_2)$$

$$S^o(12) \star \delta(\vec{r}_{12})\, T_o(12)\, S^o(12)\, e^{-i\vec{k}.\vec{r}_1} .$$

We can replace both operators $S^o(12)$ under the integral sign by $S^o(1)$ and reduce the result to

$$W(C_2) = S^o(\vec{k},1) \star n_o \Lambda^s(1)\, S^o(\vec{k},1) , \qquad \text{(II.28a)}$$

where the Lorentz-Boltzmann operator $\Lambda^s(1)$ is

$$\Lambda^s(1) = \int d\vec{v}_2\, \phi_o(v_2)\, T_o(12) . \qquad \text{(II.28b)}$$

A final simplification is obtained by using the Fourier representation of the operator C_m in (II.25b). We insert between any two successive operators S^o and $T_o(ij)$ occurring in C_m , completeness relations for plane waves of the forms

$$1 = \int .. \int d\vec{k}_1 .. d\vec{k}_m \mid \vec{k}_1 .. \vec{k}_m > < \vec{k}_1 .. \vec{k}_m \mid , \qquad \text{(II.29a)}$$

where

$$\mid \vec{k}_1 .. \vec{k}_m > = \prod_{s=1}^{m} \overline{\exp(i\vec{k}_s . \vec{r}_s)} \qquad \text{(II.29b)}$$

and

$$\bullet \quad \langle \vec{k}_1 .. \vec{k}_m \mid A(\vec{r}_1,..,\vec{r}_m) \rangle =$$

$$\int .. \int \left(\prod_{s=1}^{m} (2\pi)^{-d}\, d\vec{r}_s\, e^{-i\vec{k}_s \cdot \vec{r}_s} \right) A(\vec{r}_1,..,\vec{r}_m) \, . \qquad \text{(II.29c)}$$

As a result the operators in C_m are replaced by

$$\bullet \quad \langle \vec{k}'_1 .. \vec{k}'_m \mid T(ij) \mid \vec{k}''_1 .. \vec{k}''_m \rangle =$$

$$(2\pi)^{-d}\, T_o(ij)\, \delta(\vec{k}'_i + \vec{k}'_j - \vec{k}''_i - \vec{k}''_j) \prod_{s \neq i,j} \delta(\vec{k}'_s - \vec{k}''_s)$$

and

$$\bullet \quad \langle \vec{k}'_1 .. \vec{k}'_m \mid S^o_t \mid \vec{k}''_1 .. \vec{k}''_m \rangle = \prod_{s=1}^{m} S^o_t(\vec{k}'_s, s)\, \delta(\vec{k}'_s - \vec{k}''_s) \; ,$$

where $\delta(\vec{k}-\vec{k}')$ represents a d dimensional Dirac δ function and one has to integrate over all intermediate $\vec{k}$ vectors.

In the next section all connected ordered m particle terms C_m in equation (II.25a) for $\overline{\Gamma}^s_{\vec{k}}(1,t)$ will be represented by diagrams.

The reduction of the BCE for the fluid propagator $\overline{\Gamma}_{\vec{k}}(i,t)$ given in (II.4), to connected ordered m particle terms goes completely similar. These terms will again be represented by diagrams.

b. Diagrammatic Representations

The operators $\overline{\Gamma}^{s}_{\vec{k}}(1,t)$ and $\overline{\Gamma}_{\vec{k}}(i,t)$ defined by (II.1) and (II.4) respectively will be represented by a double straight line, labeled $(1,\vec{k})$ and $(i,\vec{k})$ respectively, as is shown on the left hand side of figure 1 , where the vertical axis is the time axis from the top (t=o) to the bottom (t) .

The operators $S^{o}_{t}(\vec{k},i)$ (i=1,2,...) (II.27) will be represented by single solid lines, labeled $(i,\vec{k})$, and the $T_o(ij)$ operators (II.21) by dots. The right hand side of figure 1 contains all diagrams, which can be built up from dots and line segments such that:

1. each diagram can only contain vertices of type 1 , 2 , 3 or 4 as is shown in figure 2 ;
2. no line segments, except one at the top and one at the bottom, have an open end;
3. the dots are labeled as they occur from the top to the bottom by an ordered set of times t_1 , t_2 , ... , and ordered time integrations are performed from t=o up to t ;
4. each line segment is labeled by a wave number and a particle label; the particles are labeled in natural order 1 , 2 , ... , m as they occure from left to right in the connected ordered m particle terms;
5. the first and the last line segment occurring in each diagram have the same wave number and particle label as $\overline{\Gamma}^{s}_{\vec{k}}(1,t)$ or $\overline{\Gamma}_{\vec{k}}(i,t)$;
6. at each dot the sum of incoming and outgoing wave numbers is the same and one integrates over all wave vectors except $\vec{k}$ each with a weightfactor $(2\pi)^{-d}$;
7. at each dot the particle label of the left incoming and left outgoing line segment is the same;
8. at each dot with two incoming and two outgoing line segments also the right incoming and outgoing line segments have the same particle label;

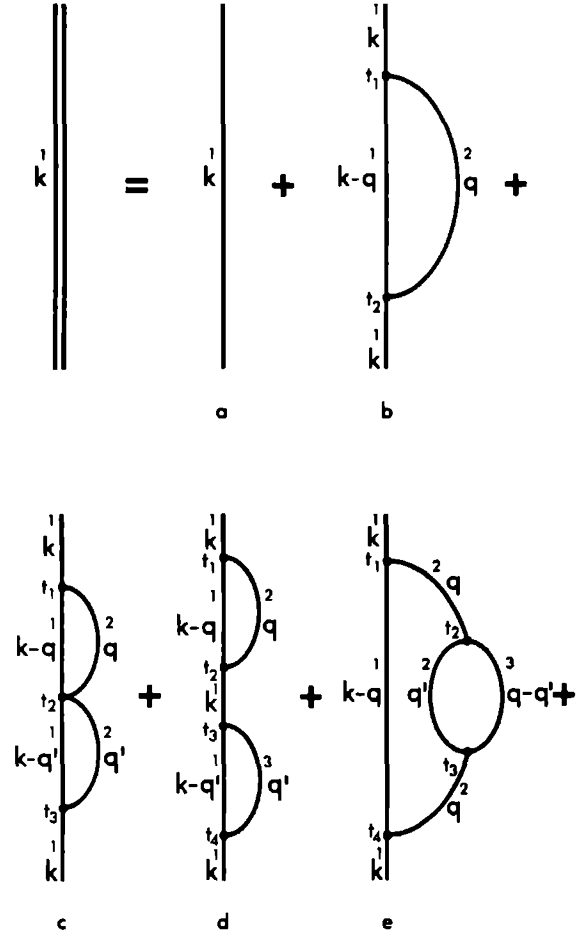


figure 1 : Diagrammatic representation of the propagator $\overline{\Gamma}^{s}_{\vec{k}}(1,t)$. The representation of $\overline{\Gamma}_{\vec{k}}(i,t)$ is obtained by replacing 1 with i .

9. at each dot with one incoming and two outgoing line segments a new particle label j has to be introduced for the right outgoing line segment and one integrates over the velocity $\vec{v}_j$ with a weight function $n_o \, \phi_o(v_j)$.

The rules how to read the diagrams are slightly different in the cases, where figure 1 represents the expansion of $\overline{\Gamma}^s$ or $\overline{\Gamma}$.
Let us first discuss the case that figure 1 stands for the diagram expansion of $\overline{\Gamma}^s_{\vec{k}}(1,t)$:

a. reading a diagram from the bottom to the top one has to write down the corresponding expression from the right to the left;
b. each dot occurring in a vertex of type 1 or 2 represents the binary collision operator $T_o(ij)$ given in (II.21), where i and j are the particle labels occurring in the vertex;
c. each dot occurring in a vertex of type 3 represents $T_o(ij)$ if i or j equals 1 (the label of the tagged particle) and represents $T_o(ij)\ (1+P_{ij})$ in all other cases, where i and j are the particle labels occurring in the vertex and the permutation operator P_{ij} interchanges the labels of particles i and j ;
d. each dot occurring in a vertex of type 4 represents the operator $n_o\Lambda^s(1)$ if i=1 and represents $n_o\Lambda(i)$ in all other cases, where i is the label occurring in the vertex; the Lorentz Boltzmann operator $\Lambda^s(1)$ is defined in (II.28b), the Boltzmann operator $\Lambda(i)$ will be defined below;
e. each line segment labeled with wave number $\vec{q}$ and particle label i between dots labeled with times t_1 and t_2 represents a free particle propagator $S^o_{t_2-t_1}(\vec{q},i)$.

Secondly if figure 1 stands for the diagram expansion of $\overline{\Gamma}_{\vec{k}}(i,t)$ with $i\neq 1$, the same five rules a. - e. are applicable except for the fact that the tagged particle label 1 is forbidden everywhere inside the

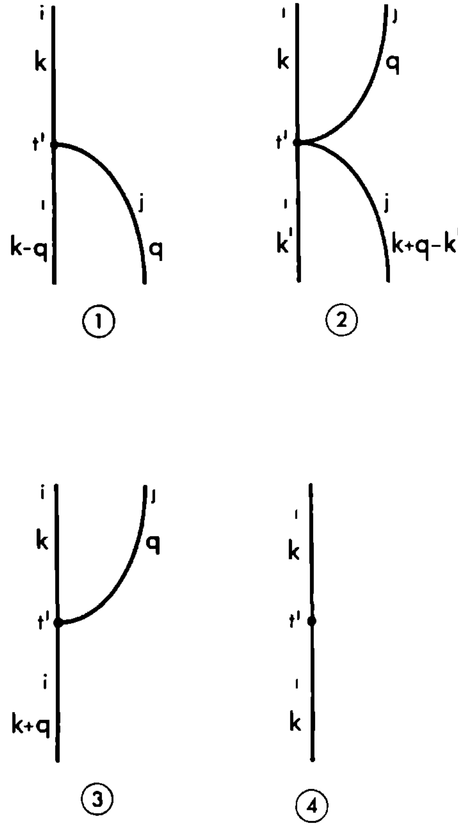


figure 2 : Types of vertices, which may occur in the diagrams representing $\overline{\Gamma}^{S}_{\vec{k}}(1,t)$ and $\overline{\Gamma}_{\vec{k}}(i,t)$.

diagrams.

For our purpose it is convenient to carry out a further resummation. Consider the Boltzmann propagator for the tagged particle $\Gamma^s_{\vec{q}}(1,t)$ and the Boltzmann propagator for a fluid particle $\Gamma_{\vec{q}}(i,t)$ defined as

$$\Gamma^s_{\vec{q}}(1,t) = \exp(L^s_{\vec{q}}(1)t) \tag{II.30a}$$

$$\Gamma_{\vec{q}}(i,t) = \exp(L_{\vec{q}}(i)t) , \tag{II.30b}$$

where

$$L^s_{\vec{q}}(1) = -i\vec{q}.\vec{v}_1 + n_o\Lambda^s(1) \tag{II.31a}$$

$$L_{\vec{q}}(i) = -i\vec{q}.\vec{v}_i + n_o\Lambda(i) . \tag{II.31b}$$

The Lorentz-Boltzmann collision operator for the self motion of a tagged particle was defined as

$$\Lambda^s(1) = \int d\vec{v}_2\, \phi_o(v_2)\, T_o(12) . \tag{II.32a}$$

The Boltzmann collision operator describing the motion of the fluid is given by

$$\Lambda(i) = \int d\vec{v}_j\, \phi_o(v_j)\, T_o(ij)\, (1+P_{ij}) . \tag{II.32b}$$

By expanding the Boltzmann propagators in Boltzmann collision operators and free streaming operators, one sees that $\Gamma^s_{\vec{q}}(1,t)$ and $\Gamma_{\vec{q}}(i,t)$ represent the sum of all diagrams, which can be built according to the previous rules, *if one allows only vertices of type 4* .
This observation can be used to resum diagrams with free streaming operators $S^o_t(\vec{q},i)$ and vertices of type 1 , 2 , 3 , 4 , to diagrams

with vertices of type 1 , 2 and 3 only, in which the free particle propagator $S_t^o(\vec{q},1)$ for the tagged particle is replaced by $\Gamma^s_{\vec{q}}(1,t)$ and in which $S_t^o(\vec{q},i)$ $(i=2,3,\ldots)$ is replaced by $\Gamma_{\vec{q}}(i,t)$.

Therefore, in the diagrams to be considered we exclude vertices of type 4 , we omit rule d. and change rule e. into e'. , reading:

e'. each line segment with wave number $\vec{q}$ and particle label i between dots labeled with times t_1 and t_2 respectively represents either the Boltzmann propagator for the tagged particle $\Gamma^s_{\vec{q}}(1,t_2-t_1)$ if $i=1$ or the Boltzmann propagator for a fluid particle $\Gamma_{\vec{q}}(i,t)$ in all other cases.

With the help of the new diagram rules the diagrammatic expansion of figure 1 can now explicitly be written down as

$$\bar{\Gamma}^s_{\vec{k}}(1,t) = \Gamma^s_{\vec{k}}(1,t) + R^s_{\vec{k}}(1,t) + \ldots , \tag{II.33a}$$

$$\bar{\Gamma}_{\vec{k}}(i,t) = \Gamma_{\vec{k}}(i,t) + R_{\vec{k}}(i,t) + \ldots . \tag{II.33b}$$

The first term on the right hand side is the weight of diagram 1a . The so called ring propagator R^s (or R) is the weight of diagram 1b and is equal to

$$R^s_{\vec{k}}(1,t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int d\vec{q}\ (2\pi)^{-d} \int d\vec{v}_2\ n_o\phi_o(v_2)$$
$$\Gamma^s_{\vec{k}}(1,t_1)\ \ T_o(12)\ \Gamma^s_{\vec{k}-\vec{q}}(1,t_2-t_1)\ \Gamma_{\vec{q}}(2,t_2-t_1)\ T_o(12)\ \Gamma^s_{\vec{k}}(1,t-t_2)\ . \tag{II.34}$$

An analogous expression holds for $R_{\vec{k}}(i,t)$.
The operator corresponding to diagram 1c is referred to as the repeated ring propagator.

c. Properties of Boltzmann propagators

In this section we study the Boltzmann propagators $\Gamma^s_{\vec{q}}$ and $\Gamma_{\vec{q}}$ defined in (II.30) in more detail.

If we define an inner product in the one particle velocity space for any two functions of $\vec{v}_i$ as

$$\cdot \quad \langle f \mid g \rangle_i = \langle f^* g \rangle_i \,, \tag{II.35}$$

where the average is defined in (II.2) and where i=1 refers to the tagged particle and i≠1 to a fluid particle, then $L^s_o(1) = n_o \Lambda^s(1)$ and $L_o(i) = n_o \Lambda(i)$ are hermitean operators, but $L^s_{\vec{q}}(1)$ and $L_{\vec{q}}(i)$ are clearly not for $\vec{q} \neq o$, as can be seen from (II.31).

We assume that in some q region around q=o the operators $L^s_{\vec{q}}$ and $L_{\vec{q}}$ have a complete set of eigenfunctions (Scharf 1969) labeled with λ and denoted by

$$\cdot \quad L^s_{\vec{q}}(1)\, \varphi^{s,\lambda}_{\vec{q}}(\vec{v}_1) = z^{s,\lambda}_{\vec{q}}\, \varphi^{s,\lambda}_{\vec{q}}(\vec{v}_1) \,, \tag{II.36a}$$

$$\cdot \quad L_{\vec{q}}(i)\, \varphi^{\lambda}_{\vec{q}}(\vec{v}_i) = z^{\lambda}_{\vec{q}}\, \varphi^{\lambda}_{\vec{q}}(\vec{v}_i) \,, \tag{II.36b}$$

where the eigenvalues are denoted by z^λ and have a non-positive real part. If q=o both spectra are real and non-positive, some eigenvalues are zero and there exists a gap between the zero eigenvalues and the first non-vanishing eigenvalue, which is of the order of the inverse mean free time (t_o^{-1}) , as is discussed extensively in reference (Foch 1970).

The operator $L^s_o(1)$ has only one eigenfunction with zero eigenvalue, the unit function. The operator $L_o(i)$ has d+2 eigenfunctions with zero eigenvalue; they are the summational invariants 1 , $\vec{v}_i$ and v_i^2 . This can immediately be proven from (II.8-10).

Using ordinary perturbation theory, where q is used as the expansion parameter, one finds one eigenfunction of $L^s_{\vec{q}}(1)$ with vanishing eigenvalue as q approaches zero. This eigenfunction is called the diffusion mode

$$\varphi^s_{\vec{q}}(\vec{v}_1) = 1 + iq\,(n_o\Lambda^s)^{-1}\,\hat{q}.\vec{v}_1 + \mathcal{O}(q^2)\ , \tag{II.37}$$

and the corresponding eigenvalue is

$$z^s_q = -D_o q^2 + \mathcal{O}(q^4)\ , \tag{II.38}$$

where the Boltzmann self diffusion coefficient is given by

$$D_o = -<v_{1x}\,(n_o\Lambda^s)^{-1}\,v_{1x}>_1\ . \tag{II.39}$$

From the fact that there is a gap of order t_o^{-1} in the spectrum of L^s_o it is clear from perturbation theory, that the concept of "diffusion mode" may only be used if $D_o q^2 t_o \ll 1$, which will be sufficient for our purposes.

Using perturbation theory for degenerate eigenvalues one obtains d+2 eigenfunctions of $L_{\vec{q}}(i)$ with eigenvalues approaching zero as q goes to zero. These are the hydrodynamic modes and corresponding hydrodynamic frequencies denoted as $\varphi^j_{\vec{q}}$ and z^j_q respectively, where j=1 , 2 , ... , d+2 . In lowest order in q they are given in refs. (Ernst 1972a; Dorfman 1972).

The heat mode in lowest order in q is given by

$$\varphi^T_{\vec{q}}(\vec{v}_i) = \{2(d+2)\}^{-\frac{1}{2}}\,\{\beta m v_i^2 - d - 2\}\ , \tag{II.40}$$

with corresponding eigenvalue

$$z_q^T = - D_{To} q^2 + \mathcal{O}(q^3) \ . \tag{II.41}$$

Here D_{To} is the (low density) Boltzmann value of the thermal diffusivity

$$D_{To} = \lambda_o/(n_o c_p) \ , \tag{II.42}$$

where λ_o is the low density value of the heat conductivity and c_p is the ideal gas specific heat per particle at constant pressure in d dimensions $c_p = k_B\,(d+2)/d$.

The two sound modes to lowest order in q are given by

$$\varphi^{\sigma}_{\vec{q}}(\vec{v}_i) = (2d(d+2))^{-\frac{1}{2}}\ \beta m \ \{\ v_i^2 + \sigma d c_o\ \hat{q}.\vec{v}_i\ \} \tag{II.43}$$

with corresponding eigenvalue

$$z_q^{\sigma} = - i\ \sigma\ c_o\ q - \tfrac{1}{2}\ \Gamma_{so}\ q^2 + \mathcal{O}(q^3) \ . \tag{II.44}$$

Here $\sigma = \pm 1$, $c_o = \{(d+2)/(\beta m d)\}^{\frac{1}{2}}$ is the ideal gas sound velocity and Γ_{so} is the low density value of the sound wave damping constant

$$\Gamma_{so} = (\gamma_o - 1)\ D_{To} + 2\,\frac{d-1}{d}\,\nu_o \ . \tag{II.45}$$

Here $\gamma_o = c_p/c_V = (d+2)/d$ and the low density value of the kinematic viscosity ν_o is equal to $\nu_o = \eta_o/(m n_o)$ where η_o is the low density value of the shear viscosity.

We will need explicitly the d-1 normalized shear modes in first order in q which are, in any dimension, given by

$$\varphi^{\eta_j}_{\vec{q}}(\vec{v}_i) = (\beta m)^{\frac{1}{2}}\ \hat{q}_\perp^{(j)}.\vec{v}_i \ +$$

$$(\beta m)^{\frac{1}{2}}\ iq\ (n_o \Lambda(i))^{-1}\ \hat{q}.\vec{v}_i\ \hat{q}_\perp^{(j)}.\vec{v}_i + \mathcal{O}(q^2) \ , \tag{II.46}$$

with corresponding eigenvalue

$$z_{q}^{\eta j} = -\nu_{o} q^{2} + O(q^{4}) \, . \tag{II.47}$$

Here j=1 , ... , d-1 and $\hat{q}_{\perp}^{(j)}$ are d-1 orthogonal unit vectors perpendicular to $\vec{q}$.

The diffusion mode (II.37) and the hydrodynamic modes (II.40,43,46) are right eigenfunctions of $L_{\vec{q}}^{s}(1)$ and $L_{\vec{q}}(i)$ respectively. Completeness relations for these operators generally involve biorthogonal sets of right and left eigenfunctions; the left eigenfunctions being the eigenfunctions of the hermitean conjugates of $L_{\vec{q}}^{s}(1)$ and $L_{\vec{q}}(i)$, given by

$$L_{\vec{q}}^{s\dagger}(1) = i\vec{q}.\vec{v}_{1} + n_{o}\Lambda^{s}(1) \, , \tag{II.48a}$$

$$L_{\vec{q}}^{\dagger}(i) = i\vec{q}.\vec{v}_{i} + n_{o}\Lambda(i) \, , \tag{II.48b}$$

where we have used the hermitean property of the operators $\Lambda^{s}(1)$ and $\Lambda(i)$.

The eigenfunctions and eigenvalues of $L_{\vec{q}}^{s\dagger}(1)$ and $L_{\vec{q}}^{\dagger}(i)$ are denoted by $\tilde{\varphi}_{\vec{q}}^{s,\lambda}$, $\tilde{z}_{\vec{q}}^{s,\lambda}$ and $\tilde{\varphi}_{\vec{q}}^{\lambda}$, $\tilde{z}_{\vec{q}}^{\lambda}$ respectively. Due to the fact that Λ^{s} and Λ are real and symmetric operators we have the properties

$$\tilde{\varphi}_{\vec{q}}^{s,\lambda} = \varphi_{\vec{q}}^{s,\lambda *} \, , \quad \tilde{z}_{\vec{q}}^{s,\lambda} = z_{\vec{q}}^{s,\lambda *} \, , \tag{II.49a}$$

$$\tilde{\varphi}_{\vec{q}}^{\lambda} = \varphi_{\vec{q}}^{\lambda *} \, , \quad \tilde{z}_{\vec{q}}^{\lambda} = z_{\vec{q}}^{\lambda *} \, . \tag{II.49b}$$

By virtue of the isotropy of Λ^{s} and Λ in $\vec{v}$ space , $z_{\vec{q}}^{s,\lambda *}$ and $z_{\vec{q}}^{\lambda *}$ are also eigenvalues of $L_{\vec{q}}^{s}$ and $L_{\vec{q}}$ respectively, with eigenfunctions $\varphi_{\vec{q}}^{s,\lambda *}(-\vec{v}_{1})$ and $\varphi_{\vec{q}}^{\lambda *}(-\vec{v}_{i})$.

The functions $\tilde{\varphi}^{s,\lambda}_{\vec{q}}$ and $\varphi^{s,\lambda}_{\vec{q}}$ form a biorthonormal set, i.e. $< \tilde{\varphi}^{s,\lambda}_{\vec{q}} \mid \varphi^{s,\lambda'}_{\vec{q}} >_1 = \delta_{\lambda,\lambda'}$, and similarly for the functions $\tilde{\varphi}^{\lambda}$ and φ^{λ}. These biorthonormal sets can be used to decompose the propagators Γ^s and Γ into

$$\cdot \quad \Gamma^s_{\vec{q}}(1,t) = \mid \varphi^s_{\vec{q}} >_1 \exp(z^s_q t) < \tilde{\varphi}^s_{\vec{q}} \mid$$

$$+ \sum_{\lambda}{}' \mid \varphi^{s,\lambda}_{\vec{q}} >_1 \exp(z^{s,\lambda}_{\vec{q}} t) < \tilde{\varphi}^{s,\lambda}_{\vec{q}} \mid \tag{II.50a}$$

$$\cdot \quad \Gamma_{\vec{q}}(i,t) = \sum_j \mid \varphi^j_{\vec{q}} >_i \exp(z^j_q t) < \tilde{\varphi}^j_{\vec{q}} \mid$$

$$+ \sum_{\lambda}{}' \mid \varphi^{\lambda}_{\vec{q}} >_i \exp(z^{\lambda}_{\vec{q}} t) < \tilde{\varphi}^{\lambda}_{\vec{q}} \mid \ , \tag{II.50b}$$

where $j=1 , \ldots , d+2$ and the prime on the summation sign indicates that λ runs over all eigenfunctions except the diffusion mode (II.50a) or the hydrodynamic modes (II.50b).
On a time scale where t is measured in units t_o and q is such that $Dq^2 t_o \ll 1$, the first term on the right hand side of (II.50a) and (II.50b) is slowly decaying in time while the second term is fastly damped. Therefore we define the projection operator on the diffusion mode as

$$\cdot \quad P^s_{\vec{q}}(1) = \mid \varphi^s_{\vec{q}} >_1 < \tilde{\varphi}^s_{\vec{q}} \mid \tag{II.51}$$

and the projection operator on the hydrodynamic modes as

$$\cdot \quad P_{\vec{q}}(i) = \sum_j P^j_{\vec{q}}(i)$$

$$\cdot \quad P^j_{\vec{q}}(i) = \mid \varphi^j_{\vec{q}} >_i < \tilde{\varphi}^j_{\vec{q}} \mid \ , \tag{II.52}$$

where $j=1 , \ldots , d+2$.

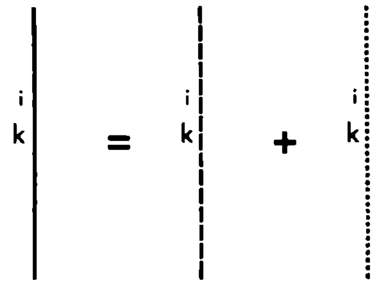


figure 3 : Decomposition of the Boltzmann propagators into a slowly and a fastly decaying part.

These projection operators can be used to divide the propagators into a slowly decaying part ($P^s_{\vec q}\, \Gamma^s_{\vec q}$ and $P_{\vec q}\, \Gamma_{\vec q}$) and a fastly decaying part ($(1-P^s_{\vec q})\, \Gamma^s_{\vec q}$ and $(1-P_{\vec q})\, \Gamma_{\vec q}$) respectively.
The operators $P^s_{\vec q}\, \Gamma^s_{\vec q}$ and $P_{\vec q}\, \Gamma_{\vec q}$ will be denoted in diagrammatic form as a dashed single straight vertical line (slow decay); the operators $(1-P^s)\, \Gamma^s$ and $(1-P)\, \Gamma$ are denoted by a dotted line (fast decay).
Figure 3 represents the equations (II.50) in diagrammatic form.
Since we are interested in long times it is sufficient for our purposes to replace the fastly decaying parts of Γ^s and Γ by properly normalized δ functions in time, and for small values of q equation (II.50a) may, therefore, approximately be written as

$$\Gamma^s_{\vec q}(1,t) \simeq P^s_{\vec q}(1) \exp(-D_o q^2 t) + (1-P^s_{\vec q}(1))\ \{ i\vec q.\vec v_1 - n_o \Lambda^s \}^{-1}\, \delta(t)\ . \qquad \text{(II.53)}$$

This expression is useful for practical calculations. When formal difficulties arise one has to use the exact formula (II.50a).
As can be verified afterwards we only need the slowly decaying part of $\Gamma_{\vec q}(i,t)$

$$P_{\vec q}(i)\ \Gamma_{\vec q}(i,t) = \sum_{j=1}^{d+2} \mid \varphi^j_{\vec q} >_i \exp(z^j_{\vec q} t) < \tilde\varphi^j_{\vec q} \mid\ . \qquad \text{(II.54)}$$

In concluding this section we mention two useful properties of the binary collision operator $T_o(ij)$ defined in (II.21).
Since the d+2 hydrodynamic modes in zeroth order in their wave number dependence are linear combinations of the summational invariants 1 , $\vec v$, v^2 one has for $q \to o$, $k \to o$

$$T_o(12)\ \{ \varphi^j_{\vec q}(\vec v_2) + \varphi^j_{\vec q}(\vec v_3) \} = o\ , \qquad \text{(II.55)}$$

$$T_o(23)\ \{ \varphi^i_{\vec k}(\vec v_2) + \varphi^i_{\vec k}(\vec v_3) \}\ \{ \varphi^j_{\vec q}(\vec v_2) + \varphi^j_{\vec q}(\vec v_3) \} = o\ . \qquad \text{(II.56)}$$

From the definition of the Lorentz-Boltzmann collision operator given in (II.32a) and the fact that the diffusion mode equals 1 in lowest order in q' it follows from (II.55) that for q→o , q'→o

$$\cdot \quad < T_o(12)\, \varphi^{j}_{\vec{q}}(\vec{v}_2)\, \varphi^{s}_{\vec{q}'}(\vec{v}_1) >_2 = - \Lambda^{s}(1)\, \varphi^{j}_{\vec{q}}(\vec{v}_1)\, \varphi^{s}_{\vec{q}'}(\vec{v}_1)$$

$$< \varphi^{j}_{\vec{q}}(\vec{v}_2)\, \varphi^{s}_{\vec{q}'}(\vec{v}_1)\, T_o(12) >_2 = - \varphi^{j}_{\vec{q}}(\vec{v}_1)\, \varphi^{s}_{\vec{q}'}(\vec{v}_1)\, \Lambda^{s}(1) \; . \qquad \text{(II.57)}$$

From the definition of the Boltzmann collision operator (II.32b) and the property (II.54) it follows that for q→o , k→o

$$\cdot \quad < T_o(23)\, (1+P_{23})\, \varphi^{i}_{\vec{k}}(\vec{v}_2)\, \varphi^{j}_{\vec{q}}(\vec{v}_3) >_3 = - \Lambda(2)\, \varphi^{i}_{\vec{k}}(\vec{v}_2)\, \varphi^{j}_{\vec{q}}(\vec{v}_2)$$

$$\cdot \quad < \varphi^{i}_{\vec{k}}(\vec{v}_2)\, \varphi^{j}_{\vec{q}}(\vec{v}_3)\, T_o(23)\, (1+P_{23}) >_3 = - \varphi^{i}_{\vec{k}}(\vec{v}_2)\, \varphi^{j}_{\vec{q}}(\vec{v}_2)\, \Lambda(2) \; . \qquad \text{(II.58)}$$

d. Diagrammatic representation for the super Burnett coefficient

The diagrammatic representation for $\overline{\Gamma}^{s}_{\vec{k}}(1,t)$, given in figure 1, and studied in the previous sections can be applied to the calculation of the velocity correlation function $\widetilde{C}(t)$ using the expression (II.6). The explicit calculations will be performed in the next two chapters. From the results one immediately obtains expressions for the time dependent diffusion coefficient $D^{(o)}(t)$ using (I.45) and the quantities $E_1(t)$, $E_2(t)$, $E_3(t)$ defined in (I.47-50).
In order to calculate, from kinetic theory, the time dependent super Burnett coefficient $D^{(2)}(t)$, given in (I.46), we have to adapt the kinetic theory given so far to the calculation of the four point velocity correlation function occurring in the expressions (I.46) and (I.47) for $D^{(2)}(t)$ and $E(t)$. The function $E(t)$, which is the ordered time integral over the four point velocity correlation function can be calculated from the same kinetic theory with slight modifications. The modifications are:

1. $E(t)$ is represented by the set of all diagrams, which can be obtained by attaching four crosses to the tagged particle line of each diagram occurring in the expansion of $\overline{\Gamma}^{s}_{o}(1,t_3)$ drawn in figure 1: one cross at the top, t=o , one cross at the bottom, t_3 , and two crosses at intermediate levels, labeled with times t_1 and t_2 .
2. One has to perform time ordered integrations from o up to t over t_1 , t_2 , t_3 and the times corresponding to the dots.
3. Each cross represents the tagged particle velocity v_{1x} and one integrates over $\vec{v}_1$ with a weight function $\phi_o(v_1)$.
4. Furthermore the diagrams have to be read according to the rules a. , b. , c. and e'. given in section *b*, where a cross is equivalent to a dot as far as rule e'. is concerned, and vertices of type 4 (see figure 2) are forbidden.

Eventually one may resum diagrams according to the expansion of figure 1.

Explicit calculations for $E(t)$ will be carried out in the next two chapters.

CHAPTER III

Kinetic theory calculations in three dimensions

a. The velocity correlation function

In this chapter we explicitly calculate the long time behaviour of the velocity correlation function and the super Burnett coefficient for a three dimensional hard sphere system at low densities.

We start in this section with the velocity correlation function given by the expression (II.6)

$$\tilde{C}(t) = \langle v_{1x}\, v_{1x}(t) \rangle = \langle v_{1x}\, \overline{\Gamma}^{s}_{o}(1,t)\, v_{1x} \rangle_1 \;. \qquad \text{(III.1a)}$$

This function is represented in diagrammatic form by the left hand side of figure 4, where the two crosses stand for the two velocities and the double straight line for $\overline{\Gamma}^{s}_{o}(1,t)$, according to figure 1. Following the expansion of figure 1 or equivalently relation (II.33a) we obtain

$$\tilde{C}(t) = \tilde{C}^{(B)}(t) + \tilde{C}^{(R)}(t) + \tilde{C}^{(c)}(t) + \tilde{C}^{(d)}(t) + \tilde{C}^{(e)}(t) + \ldots \;, \qquad \text{(III.1b)}$$

where $\tilde{C}^{(B)}(t)$ is the Boltzmann contribution to $\tilde{C}(t)$ represented by diagram a in figure 4, $\tilde{C}^{(R)}(t)$ is the ring contribution represented by diagram b, and so on.
On the right hand side of figure 4 we already applied the decomposition of the Boltzmann propagators $\Gamma^{s}_{\vec{q}}(1,t')$ and $\Gamma_{\vec{q}}(i,t')$ into a fastly and slowly decaying part according to figure 3 and relation (II.50) Using the fact that

$$P^{s}_{o}(1)\mid v_{1x} \rangle = o \;;\; \langle v_{1x} \mid P^{s}_{o}(1) = o \;, \qquad \text{(III.2)}$$

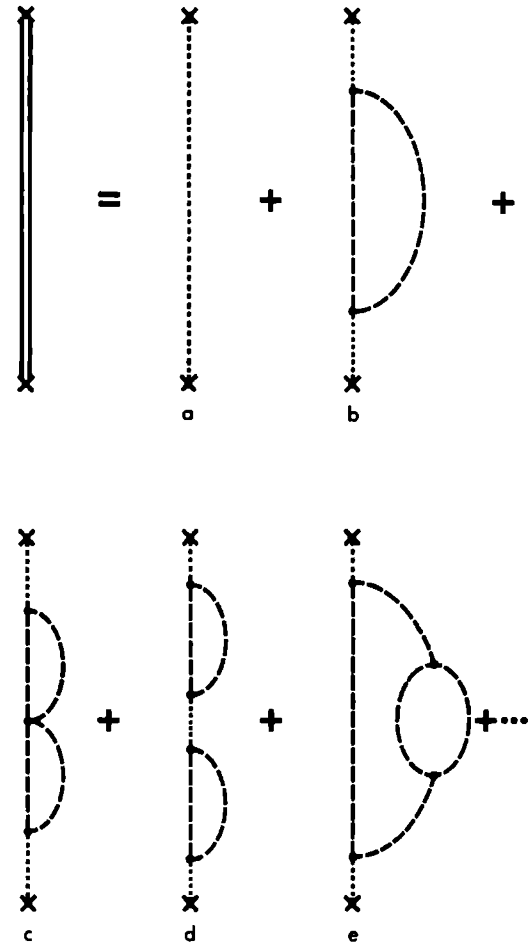


figure 4 : Various contributions to the velocity correlation function in a three dimensional system.

it is seen directly that all diagrams on the right hand side of figure 4 start and end with the fastly decaying part of the Boltmann self propagator.

The Boltzmann contribution to the velocity correlation function (diagram a in figure 4) is given by

$$\widetilde{C}^{(B)}(t) = \langle v_{1x}\, \Gamma_o^s(1,t)\, v_{1x} \rangle_1 \;. \tag{III.3}$$

Using the approximation (II.53) for $\Gamma_o^s(1,t)$ and the definition for the Boltzmann value of the linear self diffusion coefficient (II.39) we obtain

$$\widetilde{C}^{(B)}(t) = D_o\, \delta(t) \;. \tag{III.4}$$

This will be sufficient for our purposes since we are interested in long times, where the short time behaviour of $\widetilde{C}(t)$ may be represented by a properly normalized δ function in time.

It is still interesting to study the short time behaviour of $\widetilde{C}^{(B)}(t)$ in somewhat more detail.
Substitution of the exact expression (II.30) for $\Gamma_o^s(1,t)$ into (III.3) yields

$$\widetilde{C}^{(B)}(t) = \langle v_{1x}\, \exp(n_o \Lambda^s(1)t)\, v_{1x} \rangle_1 \;.$$

The function $\widetilde{C}^{(B)}(t)$ can be calculated in successive Enskog approximations, which is a well-known procedure (Chapman 1960) to solve the linearized Boltzmann equation yielding explicit expressions for the transport coefficients in lowest order in the density.
The first Enskog approximation restricts the space of functions $f(\vec{v}_1)$, where $\Lambda^s(1)$ is acting on, to the functions v_{1x} , v_{1y} , v_{1z} only.

Then $\Lambda^{s}(1)$ becomes a diagonal 3 x 3 matrix. The calculation leads directly to

$$\cdot \quad \tilde{C}^{(B)}(t) = (\beta m)^{-1} \exp(-\tfrac{2}{3}t/t_o) , \qquad (d=3) \qquad (III.5)$$

where t_o is the low density value of the mean free time

$$\cdot \quad t_o = \frac{(\beta m/\pi)^{\frac{1}{2}}}{4n_o\sigma^2} . \qquad (d=3) \qquad (III.6)$$

The time integral of (III.5) yields the value of the Boltzmann self diffusion coefficient D_o in first Enskog approximation

$$\cdot \quad [D_o]_1 = \frac{3}{2\beta m} t_o . \qquad (d=3) \qquad (III.7)$$

As is pointed out in the literature (Chapman 1960) $[D_o]_1$ differs only a few percent from D_o .
For times of order t_o the contributions of the next terms in the expansion (III.1b) turn out to be of higher order in the density, and so the expression (III.5) describes the dominant behaviour of the velocity correlation function for small time ($t \sim t_o$) and low densities. We may conclude from (III.5) that $\tilde{C}^{(B)}(t)$ is indeed fastly decaying.

Next we calculate the ring contribution to the velocity correlation function starting from the definition

$$\cdot \quad \tilde{C}^{(R)}(t) = < v_{1x} R_o^{s}(1,t) v_{1x} >_1 , \qquad (III.8)$$

where the ring propagator is given in (II.34).
From property (III.2) it is seen that only the fastly decaying parts of $\Gamma_o^{s}(1,t_1)$ and $\Gamma_o^{s}(1,t-t_2)$ in expression (II.34) enter into the ring contribution (III.8). The long time behaviour of $\tilde{C}^{(R)}(t)$ is obtained by replacing $\Gamma^{s}_{-\vec{q}}(1,t_2-t_1)$ and $\Gamma_{\vec{q}}(2,t_2-t_1)$ in (II.34) by their slowly

decaying parts as is indicated in diagram b of figure 4.
For $t \gg t_o$ one finds with the help of (II.51) and (II.52)

$$\cdot \quad \tilde{C}^{(R)}(t) = \sum_{j=1}^{5} \int_o^t dt_1 \int_{t_1}^t dt_2 \int' d\vec{q}\, (2\pi)^{-3} \exp\{ (z_q^s + z_q^j)(t_2 - t_1) \}$$

$$< v_{1x} (1-P_o^s)(-n_o\Lambda^s)^{-1} \delta(t_1)\, n_o < T_o(12)\, \varphi^j_{\vec{q}}(\vec{v}_2)\, \varphi^s_{-\vec{q}}(\vec{v}_1) >_2 >_1$$

$$< < \varphi^j_{\vec{q}}(\vec{v}_2)\, \varphi^s_{-\vec{q}}(\vec{v}_1)\, T_o(12) >_2 (1-P_o^s)(-n_o\Lambda^s)^{-1} \delta(t-t_2)\, v_{1x} >_1 . \tag{III.9}$$

The prime on the integral sign indicates that $q < k_o$, where k_o is a wave number of the order of the inverse mean free path. This cut off wave number has to be introduced since the decomposition of $\Gamma^s_{\vec{q}}$ and $\Gamma_{\vec{q}}$ into slowly and fastly decaying parts breaks down at values of q such that $D_o q^2 t_o \sim 1$ as was explained in section *c* of chapter II. In expression (III.9) the functions $\tilde{\varphi}^j_{\vec{q}}$ do not appear since we have expressed the innerproducts directly in terms of averages using (II.35) and (II.49).

To obtain the dominant long time behaviour of $\tilde{C}^{(R)}(t)$, the modes $\varphi^j_{\vec{q}}$ and $\varphi^s_{\vec{q}}$ in (III.9) may be taken in zeroth order in q as will be explained below. The property (II.57) can be applied to eliminate the Λ^s and T_o operators occurring in (III.9). By performing the time integrals we arrive at the relation

$$\cdot \quad \tilde{C}^{(R)}(t) = \sum_{j=1}^{5} n_o^{-1} (2\pi)^{-3} \int' d\vec{q}\, \{ < v_{1x}\, \varphi^j_{\vec{q}}(\vec{v}_1)\, \varphi^s_{-\vec{q}}(\vec{v}_1) >_1 \}^2$$

$$\exp\{ (z_q^j + z_q^s) t \} , \tag{III.10}$$

which is the "mode coupling formula" as it will appear in chapter V. It is obtained here on the basis of kinetic theory.
The matrix elements occurring in (III.10) can be calculated from (II. 37, 40, 43, 46). In lowest order in q we find for the amplitude of the

heat diffusion mode $< v_{1x}\, \varphi^{T}_{\vec{q}}(\vec{v}_1)\, \varphi^{S}_{\vec{q}}(\vec{v}_1) >_1 = o$, and so the heat mode does not contribute to the leading long time behaviour of $\tilde{C}^{(R)}(t)$, as we will explain now.

One could take the self diffusion mode or the heat mode in (III.9) in first order in q , which yields an extra factor q^2 in the q integral of (III.10). As can be easily seen from (III.10) by performing the q integral an extra factor q^2 gives an extra factor t^{-1} compared to the case where the two mode amplitude is non-vanishing.

This observation will frequently occur in our calculations and turns out to be very useful to estimate contributions due to higher order corrections on the hydrodynamic modes or the self diffusion mode.

For the sound modes we have from (II.43)

$$. \quad < v_{1x}\, \varphi^{\pm}_{\vec{q}}(\vec{v}_1)\, \varphi^{S}_{-\vec{q}}(\vec{v}_1) >_1 = \pm \sqrt{3/10}\, c_o\, \hat{q}_x \, . \qquad \text{(III.11a)}$$

The two sound modes contribute to $\tilde{C}^{(R)}(t)$ a term

$$. \quad \tilde{C}^{(R)}_{(+,-)}(t) = \frac{3\, c_o^2}{5n_o(2\pi)^3} \int' d\vec{q}\; \hat{q}_x^2 \cos(c_o q t)\; e^{-(D_o+\frac{1}{2}\Gamma_{so})q^2 t} , \qquad \text{(III.11b)}$$

which is for long times proportional to $t^{-\frac{1}{2}} \exp(-t/t_o')$, where $t_o' = (4D_o+2\Gamma_{so})c_o^{-2}$. Using the fact that, for low densities, Γ_{so} is of the same order of magnitude as D_o , we find from (III.6) and (III.7) that t_o' is of the order of the mean free time t_o . Therefore the sound mode contribution to $\tilde{C}^{(R)}(t)$ is a fastly decaying function of time, which may be neglected for $t >> t_o$.

The dominant long time behaviour of $\tilde{C}^{(R)}(t)$ arises from the contribution of a shear and a diffusion mode to (III.10). The matrix elements can be calculated in lowest order in q from (II.37) and (II.46), yielding

$$. \quad \sum_{j=1,2} \{ < v_{1x}\, \varphi^{\eta j}_{\vec{q}}\, \varphi^{S}_{-\vec{q}} >_1 \}^2 = (\beta m)^{-1} (1-\hat{q}_x^2) \, . \qquad \text{(III.12)}$$

By performing the q integration in (III.10) one finds the well-known long time tail in the velocity correlation function for $t \gg t_o$

$$\tilde{C}^{(R)}(t) = \frac{1}{12\,\pi^{3/2}\,\beta m n_o\,(D_o+\nu_o)^{3/2}}\,\frac{1}{t^{3/2}}\,. \tag{III.13}$$

The contributions of diagrams c and d of figure 4 to the velocity correlation function are of the same order in time ($t^{-3/2}$) as the ring contribution but the coefficients are of higher order in the density and should, therefore, consistently be neglected in this low density kinetic theory. Actually the contributions of c and d cancel each other, but there exists still other diagrams of the same order in time ($t^{-3/2}$) and higher order in the density, which will be consistently neglected.

The contribution to $\tilde{C}(t)$ describing the next dominant time behaviour arises from diagram e in figure 4, and reads

$$\begin{aligned}\tilde{C}^{(e)}(t) = &\int_o^t dt_1 \int_{t_1}^t dt_2 \int' d\vec{k}\,(2\pi)^{-3}\, n_o < v_{1x}\,\delta(t_1)\,(-n_o\Lambda^s)^{-1} \\ &< T_o(12) \mid \varphi^s_{-\vec{k}}(\vec{v}_1) >_1 e^{-D_o k^2(t_2-t_1)} < \tilde{\varphi}^s_{-\vec{k}}(\vec{v}_1) \mid \Upsilon_{\vec{k}}(2,t_2-t_1)\,T_o(12) >_2 \\ &\delta(t-t_2)\,(-n_o\Lambda^s)^{-1}\, v_{1x} >_1 .\end{aligned} \tag{III.14}$$

The propagator $\Upsilon_{\vec{k}}(2,t)$, representing the side branch in figure 4e, is given in Laplace language as

$$\begin{aligned}\Upsilon_{\vec{k}z}(2) = &\sum_i \mid \varphi^{\eta_i}_{\vec{k}}(\vec{v}_2) >_2 (z+\nu_o k^2)^{-1} < \tilde{\varphi}^{\eta_i}_{\vec{k}}(\vec{v}_2) \mid \\ &\sum_{\lambda,\mu} \int' d\vec{q}\,(2\pi)^{-3}\,(z-z_q^\lambda-z_l^\mu)^{-1}\, n_o < T_o(23)\,\varphi^\lambda_{\vec{q}}(\vec{v}_2)\,\varphi^\mu_{\vec{l}}(\vec{v}_3) >_2 >_3 \\ &<< \varphi^\lambda_{\vec{q}}(\vec{v}_2)\,\varphi^\mu_{\vec{l}}(\vec{v}_3)\,T_o(23)\,(1+P_{23}) >_3 \sum_j \mid \varphi^{\eta_j}_{\vec{k}}(\vec{v}_2) >_2 (z+\nu_o k^2)^{-1} < \tilde{\varphi}^{\eta_j}_{\vec{k}}(\vec{v}_2) \mid ,\end{aligned} \tag{III.15}$$

where $\vec{l} = \vec{k} - \vec{q}$, the indices i and j run over the shear modes and λ and μ run over all five hydrodynamic modes of (II.54). By using the properties (II.58), for the full Boltzmann operator, eq. (III.15) can be written as

$$\Upsilon_{\vec{k}z}(2) = \sum_{i,j} | \varphi_{\vec{k}}^{\eta_i}(\vec{v}_2) >_2 (z+\nu_o k^2)^{-1} \tfrac{1}{2}n_o \sum_{\lambda,\mu} \int' d\vec{q}\,(2\pi)^{-3}$$
$$(z-z_q^{\lambda}-z_l^{\mu})^{-1} < \varphi_{\vec{k}}^{\eta_i} \Lambda\, \varphi_{\vec{q}}^{\lambda} \varphi_{\vec{l}}^{\mu} >_2 < \varphi_{\vec{q}}^{\lambda} \varphi_{\vec{l}}^{\mu} \Lambda\, \varphi_{\vec{k}}^{\eta_j} >_2 (z+\nu_o k^2)^{-1} < \tilde{\varphi}_{\vec{k}}^{\eta_j}(\vec{v}_2) \qquad \text{(III.16)}$$

as has been shown by Ernst and Dorfman (Ernst 1972a).

The averages in (III.16) can be evaluated by means of (II.46), yielding

$$< \varphi_{\vec{q}}^{\lambda} \varphi_{\vec{l}}^{\mu} \Lambda\, \varphi_{\vec{k}}^{\eta_j} >_2 = ik\, n_o^{-1} A_{\eta_j}^{\lambda\mu}(\hat{q},\vec{l}) \, , \qquad \text{(III.17)}$$

where $A_{\eta_j}^{\lambda\mu}(\hat{q},\vec{l})$ is a two mode amplitude

$$A_{\eta_j}^{\lambda\mu}(\hat{q},\vec{l}) = (\beta m)^{\frac{1}{2}} < \varphi_{\vec{q}}^{\lambda} \varphi_{\vec{l}}^{\mu}\, \hat{k}.\vec{v}_2\, \hat{k}_1^{(j)}.\vec{v}_2 >_2 . \qquad \text{(III.18)}$$

Eq. (III.16) reduces now to

$$\Upsilon_{\vec{k}z}(2) = -k^2 \sum_{i} | \varphi_{\vec{k}}^{\eta_i}(\vec{v}_2) >_2 (z+\nu_o k^2)^{-2} < \tilde{\varphi}_{\vec{k}}^{\eta_i}(\vec{v}_2) |$$
$$\left[\tfrac{1}{2}n_o \sum_{\lambda,\mu} \int' d\vec{q}\,(2\pi)^{-3} \, |A_{\eta_j}^{\lambda\mu}(\hat{q},\vec{l})|^2 \,(z-z_q^{\lambda}-z_l^{\mu})^{-1} \right] . \qquad \text{(III.19)}$$

The dominant contributions to $\Upsilon_{\vec{k}}(2,t)$ come from z values, which are proportional to k^2 . In the factor [...] on the second line of (III.19) we may therefore replace z by a quantity of order k^2 . The resulting expression has been calculated by Ernst and Dorfman, who have shown that for $z = O(k^2)$ only two opposite sound modes contribute in the sum over λ , μ .

The result is

$$[\ldots] = a - \Delta_\eta(1)\, k^{\frac{1}{2}} \,, \qquad \text{(III.20)}$$

where a is some constant, and

$$\Delta_\eta(1) = \frac{c_o^{1/2}}{77\,\pi\, 2^{1/2}\, \beta m n_o\, \Gamma_{so}^{3/2}} \,. \qquad \text{(III.21)}$$

The constant a appearing on the right hand side of (III.20) is a higher density correction to the ring diagram in figure 4b, which replace ν_o in (III.13) by ν_o+a , and it should be neglected since we restrict ourselves consistently to the lowest order in the density. Inversion of the Laplace transform in (III.19) yields

$$T_{\vec{k}}(2,t) \simeq \Delta_\eta(1)\, k^{5/2}\, t\, e^{-\nu_o k^2 t} \sum_i |\, \varphi_{\vec{k}}^{\eta_i} >_2 < \tilde{\varphi}_{\vec{k}}^{\eta_i} \,| \,. \qquad \text{(III.22)}$$

Inserting this result in (III.14) and carrying out the remaining integrations yields finally for t >> t_o

$$\tilde{C}^{(e)}(t) = \frac{\Delta_\eta(1)\, \Gamma(11/4)}{6\,\pi^2\, \beta m n_o\, (D_o+\nu_o)^{11/4}}\, \frac{1}{t^{7/4}} \,, \qquad \text{(III.23)}$$

where $\Gamma(x)$ is the gammafunction.

The next order contributions to $\tilde{C}(t)$ arise from diagrams in which e.g. the slow Boltzmann propagator of the third particle in figure 4e is replaced by the ring propagator. One finds in this way contributions to $\tilde{C}(t)$, which are proportional to $t^{-2+2^{-n}}$ with $n = 4,5,\ldots,\infty$. This result was first obtained by Pomeau (Pomeau 1973), from hydrodynamic considerations.

The final result for $\tilde{C}(t)$ follows from (III.4,13,23)

$$\tilde{C}(t) = D_o\, \delta(t) + \frac{1}{12\,\pi^{3/2}\, \beta m n_o\, (D_o+\nu_o)^{3/2}}\, \frac{1}{t^{3/2}} +$$

$$\frac{\Delta_\eta(1)\,\Gamma(11/4)}{6\,\pi^2\,\beta m n_o\,(D_o+\nu_o)^{11/4}}\,\frac{1}{t^{7/4}}+\mathcal{O}\!\left(\frac{1}{t^{15/8}}\right)\;. \qquad (d=3) \qquad \text{(III.24a)}$$

This expression describes the behaviour of $\tilde{C}(t)$ for values of t much larger than t_o .

The time dependent diffusion coefficient $D^{(o)}(t)$, defined in (I.32), can be calculated from relation (I.45) and the results obtained so far for the velocity correlation function.
The limiting value $\lim_{t\to\infty} D^{(o)}(t)$ for low densities may be obtained according to eq. (III.24a) from the time integral over $\tilde{C}^{(B)}(t)$ and all other contributions may be neglected since they are of higher order in the density.
The deviation from that limiting value for long times arises from the contribution $\tilde{C}^{(R)}(t)$ (in eq. (III.13)) and $\tilde{C}^{(e)}(t)$ (in eq. (III.23)). We find for $D^{(o)}(t)$ for $t \gg t_o$

$$D^{(o)}(t) = D_o - \frac{1}{6\,\pi^{3/2}\,\beta m n_o\,(D_o+\nu_o)^{3/2}}\,\frac{1}{t^{1/2}}$$

$$-\frac{2\,\Delta_\eta(1)\,\Gamma(11/4)}{9\,\pi^2\,\beta m n_o\,(D_o+\nu_o)^{11/4}}\,\frac{1}{t^{3/4}}+\mathcal{O}\!\left(\frac{1}{t^{7/8}}\right)\;. \qquad (d=3) \qquad \text{(III.24b)}$$

b. The time dependent super Burnett coefficient

In this section we calculate the time dependent super Burnett coefficient from kinetic theory for a three dimensional hard sphere system.

We start from the relations (I.46-50)

$$D^{(2)}(t) = E(t) - E_1(t) - E_2(t) - E_3(t) \tag{III.25a}$$

and the diagram expansion for E(t) given in section *d* of chapter II. The functions $E_i(t)$ (i=1,2,3) can be calculated from the result for the velocity correlation function (III.24a). We derive straightforwardly for $t \gg t_o$ and d=3

$$E_1(t) = D_o^2 t - \frac{2D_o}{3\,\pi^{3/2}\,\beta m n_o\,(D_o+\nu_o)^{3/2}}\,t^{1/2}$$

$$- \frac{16\,\Delta_\eta(1)\,D_o\,\Gamma(11/4)}{9\,\pi^2\,\beta m n_o\,(D_o+\nu_o)^{11/4}}\,t^{1/4} + O(t^{1/8}) \tag{III.25b}$$

$$E_2(t) = O(\log t) \tag{III.25c}$$

$$E_3(t) = \frac{D_o}{6\,\pi^{3/2}\,\beta m n_o\,(D_o+\nu_o)^{3/2}}\,t^{1/2}$$

$$+ \frac{2\,\Delta_\eta(1)\,D_o\,\Gamma(11/4)}{3\,\pi^2\,\beta m n_o\,(D_o+\nu_o)^{11/4}}\,t^{1/4} + O(t^{1/8})\ . \tag{III.25d}$$

The diagrams contributing to E(t) as defined in section *d* of chapter II are divided into five classes (I,II,III,IV,V), drawn schematically in figure 5.
The double straight line is the full propagator $\overline{\Gamma}_o^s(1,t)$ defined in (II.1) and represents the expansion given in figure 1. The bubbles stand for the sum of all diagrams with one or two crosses in their interior

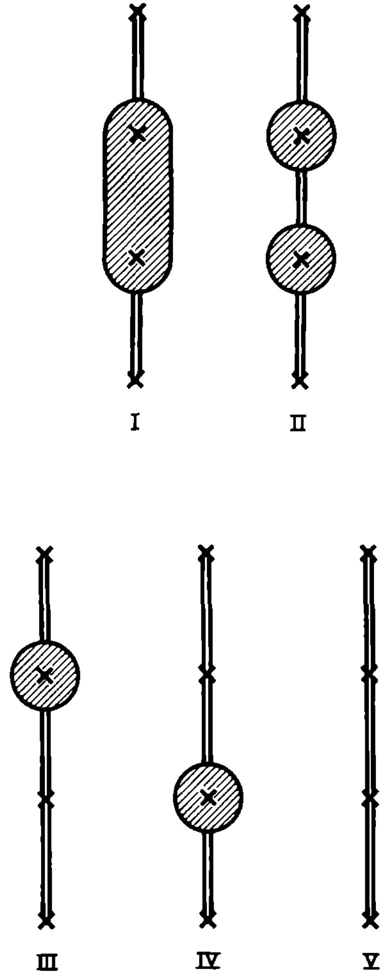


figure 5 : Classes of diagrams contributing to the super Burnett coefficient.

and will be considered below.

Let us first derive a useful property of the full propagator $\overline{\Gamma}^s_o$ from the kinetic theory of chapter II and the results of the previous section. From the fact that the operator $T_o(ij)$ acting on the unit function gives zero, as can be seen from (II.10, 21), we find from (II.30a, 31a, 32a, 51, 37) for the q=o limit of the Boltzmann propagator $\Gamma^s_{\vec{q}}(1,t)$

$$P^s_o(1)\,\Gamma^s_o(1,t) = P^s_o(1)\;;\;\Gamma^s_o(1,t)\,P^s_o(1) = P^s_o(1) \tag{III.26}$$

and for the q=o limit of the ring propagator $R^s_{\vec{q}}(1,t)$ and all further operators occurring in the expansion of $\overline{\Gamma}^s_o(1,t)$, according to figure 1

$$P^s_o(1)\,R^s_o(1) = o\;;\;R^s_o(1)\,P^s_o(1) = o \tag{III.27}$$

$$\ldots\ldots\ldots\ldots\ldots\;;\;\ldots\ldots\ldots\ldots\ldots\ldots\,.$$

Clearly the unit function, on which $P^s_o(1)$ actually projects, is an exact eigenfunction of the full propagator $\overline{\Gamma}^s_o(1,t)$ with eigenvalue 1 . This can be seen more directly from the defining equation (II.1). Therefore we have

$$P^s_o(1)\,\overline{\Gamma}^s_o(1,t) = P^s_o(1)\;;\;\overline{\Gamma}^s_o(1,t)\,P^s_o(1) = P^s_o(1)\,. \tag{III.28}$$

Therefore, the full propagator $\overline{\Gamma}^s_o(1,t)$ can be separated into a constant part and a remainder, referred to as orthogonal part

$$\overline{\Gamma}^s_o(1,t) = P^s_o(1) + (1-P^s_o(1))\,\overline{\Gamma}^s_o(1,t)\,. \tag{III.29}$$

The constant part is the most important one since it does not decay at all in time.
An estimate for the time decay of the orthogonal part can be obtained

from the results of the previous section.
The orthogonal part of the Boltzmann propagator $(1-P_o^s)\ \Gamma_o^s(1,t)$ decays exponentially in time as discussed in (III.3-7).
The orthogonal part of the ring propagator can be estimated from (III.8) and (III.13) to be of order

$$R_o^s(1,t) \sim f(t)\ (1-P_o^s)\ U(1)\ (1-P_o^s)\ . \tag{III.30}$$

Here f(t) is some bounded function of time with a leading asymptotic behaviour for large t proportional to $t^{-3/2}$ and U(1) is some regular time independent operator in one particle space.
All other operators occurring in the expansion of $\overline{\Gamma}_o^s(1,t)$ as given in figure 1, decay also at least proportional to $t^{-3/2}$ as follows from our considerations of the diagram expansion in the previous section.
Therefore the orthogonal part of $\overline{\Gamma}_o^s(1,t)$ may be estimated as

$$(1-P_o^s)\ \overline{\Gamma}_o^s(1,t) \sim f(t)\ (1-P_o^s)\ U(1)\ (1-P_o^s)\ , \tag{III.31}$$

where f(t) and U(1) have the same meaning as in (III.30).

We now consider the diagrams contributing to E(t) and divide them into five classes (I,II,III,IV,V) drawn in figure 5, namely

$$E(t) = E_{(I)}(t) + \ldots + E_{(V)}(t) \tag{III.32}$$

and we will study the classes successively.

All diagrams of class V together give a contribution to E(t) equal to

$$E_{(V)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3$$

$$< v_{1x}\ \overline{\Gamma}_o^s(1,t_1)\ v_{1x}\ \overline{\Gamma}_o^s(1,t_2-t_1)\ v_{1x}\ \overline{\Gamma}_o^s(1,t_3-t_2)\ v_{1x} >_1\ . \tag{III.33}$$

Due to the property (III.2) the propagators $\overline{\Gamma}^s_o(1,t_1)$ and $\overline{\Gamma}^s_o(1,t_3-t_2)$ in this expression may be replaced by their orthogonal parts.
If we insert for $\overline{\Gamma}^s_o(1,t_2-t_1)$ the decomposition (III.29) we find

$$\cdot \quad E_{(V)}(t) = E_{(V.A)}(t) + E_{(V.B)}(t) \ , \qquad \text{(III.34)}$$

where $E_{(V.A)}(t)$ arises from the constant part of $\overline{\Gamma}^s_o(1,t_2-t_1)$ and $E_{(V.B)}(t)$ from the orthogonal part.
It is easy to see from the relations (I.47,48), (II.6) and (III.33) that

$$\cdot \quad E_{(V.A)}(t) = E_1(t) \ , \qquad \text{(III.35)}$$

which is an exact relation valid for all times.
The behaviour of $E_1(t)$ for $t >> t_o$ is given in (III.25b).
The function $E_{(V.A)}(t)$ is by itself the most important contribution to $E(t)$, but in the calculation of $D^{(2)}(t)$, it cancels the subtracted term $E_1(t)$, according to (III.25a).
The behaviour of $E_{(V.B)}(t)$ for $t >> t_o$ can be obtained from (III.31)

$$\cdot \quad E_{(V.B)}(t) \sim \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \ f(t_1)\ f(t_2-t_1)\ f(t_3-t_2) \ ,$$

which is finite as t approaches infinity, as can be seen easily by taking the Laplace transform of this expression. So we have for $t >> t_o$

$$\cdot \quad E_{(V.B)}(t) = \mathcal{O}(1) \ . \qquad \text{(III.36)}$$

We conclude therefore that only those diagrams of class V , which are contained in subclass VA give a divergent contribution tot $E(t)$ equal to (III.35).

The dominant *short* time behaviour of $E(t)$, for low densities, is also given by diagram V (figure 5), if one replaces $\overline{\Gamma}^s_o$ by Γ^s_o similar to

(III.3-7), yielding for $t \sim t_o$

$$\cdot \quad E(t) \simeq \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3$$

$$< v_{1x}\, \Gamma_o^s(1,t_1)\, v_{1x}\, \Gamma_o^s(1,t_2-t_1)\, v_{1x}\, \Gamma_o^s(1,t_3-t_2)\, v_{1x} >_1 \quad , \text{(III.37a)}$$

which can be calculated explicitly in successive Enskog approximations and compared with computer simulation experiments.
Using standard kinetic theory we find in first Enskog approximation after lengthy but straightforward calculations, for the short time behaviour of $D^{(2)}(t)$

$$\cdot \quad D^{(2)}(t) \simeq [D_o^{(2)}]_1 \ \{ 1 + \frac{(d+1)(d^2+2d-4)}{d^3} \exp(-\lambda_o t) +$$

$$- \frac{(d-1)(d+2)^3}{2d^3} \exp(- \frac{2(d+1)}{d+2} \lambda_o t) + \frac{d+1}{2} \exp(-2\lambda_o t) +$$

$$- \frac{2(d^2-1)}{d^2} \lambda_o t \exp(-\lambda_o t) - \frac{d+1}{2d} (\lambda_o t)^2 \exp(-\lambda_o t) \ \} \ , \qquad \text{(III.37b)}$$

where d is the dimensionality of the system (here d=3) , $D_o^{(2)}$ is the Boltzmann value of the super Burnett coefficient, which in first Enskog approximation is given by

$$\cdot \quad [D_o^{(2)}]_1 = \frac{2}{d+1} (\beta m)^{-2} \lambda_o^{-3} \ , \qquad \text{(III.37c)}$$

and λ_o is for d=3 given by

$$\cdot \quad \lambda_o = \frac{2}{3t_o} \ . \qquad \text{(III.37d)}$$

The mean free time t_o is given in (III.6).

The expression (III.37b) is mainly given to illustrate qualitatively

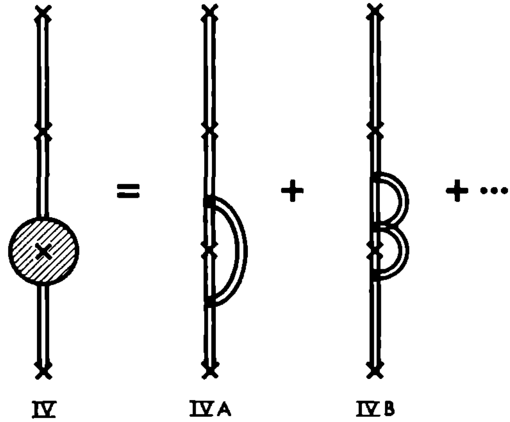


figure 6 : Decomposition of class IV into sub-classes.

the short time behaviour of $D^{(2)}(t)$, which grows very slowly, behaving initially as $\sim t^4$, and after $t = 8t_o$ ($t = 10t_o$) it has reached only 85% (95%) of its asymptotic value.
The first Enskog approximation (III.37c) does not describe quantitatively the short time behaviour of $D^{(2)}(t)$, since the Enskog approximation scheme converges slowly for the super Burnett coefficient (Wood, private communication).

Let us now pass on to class IV in figure 5.
The sum of all diagrams of class IV is equal to

$$\cdot \quad E_{(IV)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \int_{t_3}^t dt_4$$

$$< v_{1x} \overline{\Gamma}_o^s(t_1) \; v_{1x} \; \overline{\Gamma}_o^s(t_2-t_1) \; \overline{B}(t_3-t_2) \; \overline{\Gamma}_o^s(t_4-t_3) \; v_{1x} >_1 \; , \qquad \text{(III.38a)}$$

where the operator $\overline{B}$, acting on functions of $\vec{v}_1$ only, represents the bubble containing one cross, in figure 5 IV.
The series expansion of this bubble operator

$$\cdot \quad \overline{B}(t) = \overline{B}_{(A)}(t) + \overline{B}_{(B)}(t) + \ldots \qquad \text{(III.38b)}$$

gives a decomposition of class IV into subclasses IVA, IVB, ...
as is drawn in figure 6.
Note that all external propagators and $\overline{B}$ in the expressions (III.38) may be replaced by their orthogonal parts because of the property (III.2) and the fact that $\overline{B}$ always starts and ends with the operator $T_o(12)$.

The sum of all diagrams of subclass IV A is equal to $E_{(IV.A)}(t)$ given by the same expression as (III.38a) if $\overline{B}(t_3-t_2)$ is replaced by

$$\cdot \quad \overline{B}_{(A)}(t_3-t_2) = \int_{t_2}^{t_3} dt_2' \int d\vec{q} \; (2\pi)^{-3} \; n_o$$

$$< T_o(12)\, \overline{\Gamma}_{-\vec{q}}(2,t_3-t_2)\, \overline{\Gamma}^{s}_{\vec{q}}(1,t_2'-t_2)\, v_{1x}\, \overline{\Gamma}^{s}_{\vec{q}}(1,t_3-t_2')\, T_o(12) >_2 . \tag{III.39}$$

If we insert in this expression the Boltzmann propagators $\Gamma_{-\vec{q}}$ and $\Gamma^{s}_{\vec{q}}$ instead of the full propagators we obtain the kinetic operator $B_{(A)}(t_3-t_2)$ drawn in figure 7.
To obtain the long time behaviour of this operator we insert for the Boltzmann propagator of the fluid particle its slowly decaying part (II.54). Of this slow part only the shear modes will contribute due to arguments similar to those below (III.10).
The self propagators occurring in $B_{(A)}$ can be decomposed into a slowly and fastly decaying part, following figure 3, as is indicated in figure 7, so that $B_{(A)}$ falls apart into 4 terms

$$B_{(A)}(t) = B_{(A.ss)}(t) + B_{(A.fs)}(t) + B_{(A.sf)}(t) + B_{(A.ff)}(t) ,$$

which are estimated now.

If for both self propagators the slow decay is taken, (diagram (ss) of figure 7) we find

$$\begin{aligned} B_{(A.ss)}(t_3-t_2) = & \int_{t_2}^{t_3} dt_2' \int d\vec{q}\, (2\pi)^{-3} \sum_{j=1,2} \exp\{-(\nu_o+D_o)q^2(t_3-t_2)\} \\ & n_o < T_o(12)\, \varphi^{s}_{\vec{q}}(\vec{v}_1)\, \varphi^{\eta j}_{\vec{q}}(\vec{v}_2) >_1 >_2 < \varphi^{s}_{\vec{q}}(\vec{v}_1)\, v_{1x}\, \varphi^{s}_{\vec{q}}(\vec{v}_1) >_1 \\ & < < \varphi^{s}_{\vec{q}}(\vec{v}_1)\, \varphi^{\eta j}_{-\vec{q}}(\vec{v}_2)\, T_o(12) >_2 , \end{aligned} \tag{III.40}$$

where from (II.37) and (II.39) it follows that

$$< \varphi^{s}_{\vec{q}}(\vec{v}_1)\, v_{1x}\, \varphi^{s}_{\vec{q}}(\vec{v}_1) >_1 = -2iq_x D_o + O(q^2) . \tag{III.41}$$

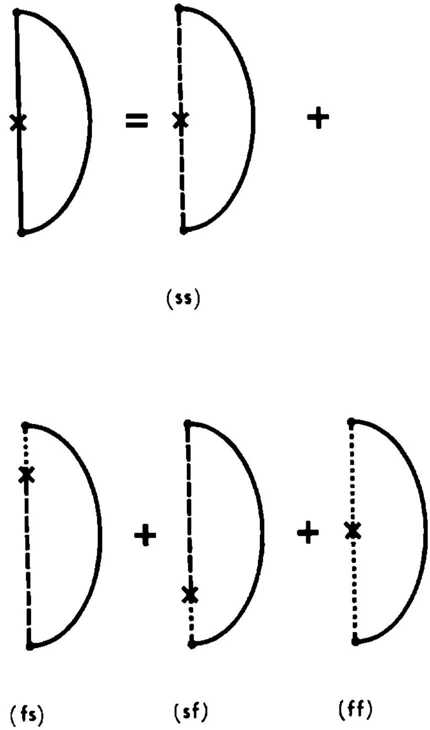


figure 7 : Decomposition of the operator $B_{(A)}(t)$ occurring in diagrams of subclass IVA.

So, at least one extra factor of order q enters the $\vec{q}$ integration, which will give an extra factor $(t_3-t_2)^{-\frac{1}{2}}$ if the q integral is performed. The other matrix elements of (III.40) are at most equal to a constant if q approaches zero, and so we estimate the operator $B_{(A,ss)}$ by performing the integrals over t_2' and $\vec{q}$ with the result

$$\cdot \quad B_{(A,ss)}(t_3-t_2) \sim g(t_3-t_2)\ (1-P_o^s)\ U'(1)\ (1-P_o^s)\ , \qquad \text{(III.42)}$$

where g(t) is a bounded function of time with a leading asymptotic behaviour for large t at most proportional to t^{-1} , and U'(1) is some regular time independent operator in one particle space.
Similar arguments can be applied to the operator $B_{(A.fs)}(t_3-t_2)$, represented by diagram (fs) in figure 7. In that case no extra factor q enters the q integration but there is a $\delta(t_2'-t_2)$ involved in the t_2' integral and therefore we may estimate

$$\cdot \quad B_{(A.fs)}(t_3-t_2) \sim f(t_3-t_2)\ (1-P_o^s)\ U''(1)\ (1-P_o^s)\ ,$$

where f(t) and U''(1) are taken in the sense of (III.30).
It is clear that the same estimate holds for the operator $B_{(A.sf)}(t_3-t_2)$ occurring in figure 7.
The last operator of this set of four satisfies

$$\cdot \quad B_{(A.ff)}(t_3-t_2) \sim \delta(t_3-t_2)\ (1-P_o^s)\ U''(1)\ (1-P_o^s)\ .$$

Therefore we conclude that the leading behaviour for long times of the operator $B_{(A)}(t)$ drawn in figure 7 and defined below (III.39) arises from the contribution $B_{(A,ss)}(t)$ (III.40) estimated in (III.42)

$$\cdot \quad B_{(A)}(t) \sim g(t)\ (1-P_o^s)\ U'(1)\ (1-P_o^s)\ , \qquad \text{(III.43)}$$

where g(t) and U'(1) are taken in the sense of (III.42).

We can dress the Boltzmann propagators in figure 7 with ring propagators, repeated ring propagators and so on, according to figure 1, to obtain an estimate of the full $\overline{B}_{(A)}$ operator in (III.38b) and we find that $B_{(A)}$ still describes the leading time behaviour of $\overline{B}_{(A)}$.
Applying the same procedure to the operators $\overline{B}_{(B)}$, ... occurring in figure 6 and the expression (III.38b), one finds an estimate for the complete bubble operator with one cross

$$\cdot \quad \overline{B}(t) \sim g(t)\ (1-P_o^s)\ U'(1)\ (1-P_o^s) \quad , \qquad \text{(III.44)}$$

where g(t) and U'(1) are taken in the sense of (III.42). The leading time behaviour of the bubble operator arises from the operator $B_{(A,ss)}$ given in (III.40).

From the result (III.44) we can estimate the sum of all diagrams of class IV.
Using (III.38a) and (III.31) we obtain

$$\cdot \quad E_{(IV)}(t) \sim \int_o^t dt_1 \ldots \int_{t_3}^t dt_4\ f(t_1)\ f(t_2-t_1)\ g(t_3-t_2)\ f(t_4-t_3)\ .$$

From the Laplace transform of this expression one derives immediately that the dominant behaviour is at most for $t >> t_o$

$$\cdot \quad E_{(IV)}(t) = \mathcal{O}(\log t)\ , \qquad \text{(III.45)}$$

which is our final result for class IV.

It is clear from figure 5 that the same estimate holds for the sum of all diagrams of class III and $t >> t_o$

$$\cdot \quad E_{(III)}(t) = \mathcal{O}(\log t)\ . \qquad \text{(III.46)}$$

The sum of all diagrams of class II give a contribution to E(t) equal to

$$\cdot \quad E_{(II)}(t) = \int_{o}^{t} dt_1 \; \dots \int_{t_4}^{t} dt_5$$

$$< v_{1x} \; \overline{\Gamma}_o^s(t_1) \; \overline{B}(t_2-t_1) \; \overline{\Gamma}_o^s(t_3-t_2) \; \overline{B}(t_4-t_3) \; \overline{\Gamma}_o^s(t_5-t_4) \; v_{1x} >_1 \; .$$

All operators occurring in this expression may be replaced by their orthogonal parts and the estimates (III.31) and (III.44) may be applied

$$\cdot \quad E_{(II)}(t) \sim \int_{o}^{t} dt_1 \; \dots \int_{t_4}^{t} dt_5 \; f(t_1) \; g(t_2-t_1) \; f(t_3-t_2) \; g(t_4-t_3) \; f(t_5-t_4)$$

and we obtain the final result for class II if $t \gg t_o$

$$\cdot \quad E_{(II)}(t) = O((\log t)^2) \; . \tag{III.47}$$

The set of diagrams belonging to class I may be decomposed into subclasses IA, IB, ... according to figure 8.
Let us first consider diagram IA.1 of class IA given in figure 9, where all full propagators are replaced by their Boltzmann equivalents. Diagram IA.1 gives a contribution to E(t) equal to

$$\cdot \quad E_{(IA.1)}(t) = \int_{o}^{t} dt_1 \; \dots \int_{t_4}^{t} dt_5 \int d\vec{q} \; (2\pi)^{-3} \; n_o < v_{1x} \; \Gamma_o^s(t_1)$$

$$< T_o(12) \; \Gamma_{-\vec{q}}(2,t_4-t_1) \; \Gamma_{\vec{q}}^s(t_2-t_1) \; v_{1x} \; \Gamma_{\vec{q}}^s(t_3-t_2) \; v_{1x}$$

$$\Gamma_{\vec{q}}^s(t_4-t_3) \; T_o(12) >_2 \Gamma_o^s(t_5-t_4) \; v_{1x} >_1 \; . \tag{III.48}$$

The Boltzmann self propagators are again decomposed into a slow and a fast part and we obtain 8 contributions to $E_{(IA.1)}(t)$ as indicated in figure 9. Note that the first and the last propagator in each diagram is always fastly decaying.

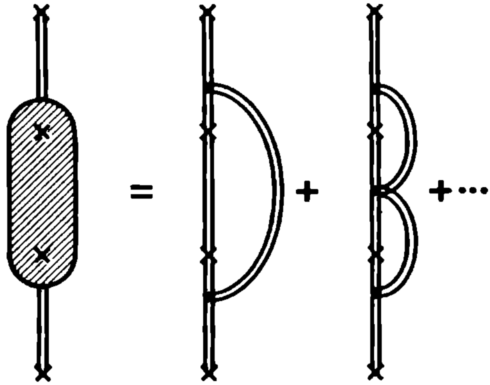


figure 8 : Decomposition of class I into sub-classes.

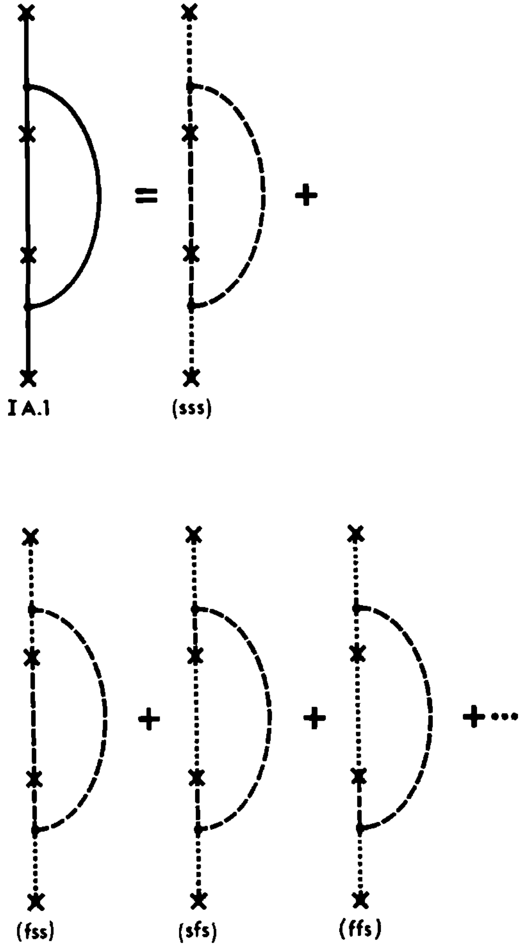


figure 9 : Decomposition of the diagram IA.1 belonging to subclass IA.

Since we are interested in long times, the slow part of the propagator of the fluid particle is taken, according to (II.54) and only the shear modes have to be taken into account.
Let us calculate the first of those 8 contributions

$$\cdot \quad E_{(IA.1sss)}(t) = \int_0^t dt_1 \, \dots \int_{t_4}^t dt_5 \int' d\vec{q} \, (2\pi)^{-3} \sum_{j=1,2}$$

$$\exp\{-(\nu_o+D_o)q^2(t_4-t_1)\} \; n_o < v_{1x} \, \delta(t_1) \, (-n_o\Lambda^s)^{-1}$$

$$< T_o(12) \, \varphi^{\eta j}_{-\vec{q}}(\vec{v}_2) \, \varphi^{s}_{\vec{q}}(\vec{v}_1) >_2 >_1 \; (< \varphi^{s}_{\vec{q}} \, v_{1x} \, \varphi^{s}_{\vec{q}} >_1)^2$$

$$< < \varphi^{\eta j}_{-\vec{q}}(\vec{v}_2) \, \varphi^{s}_{\vec{q}}(\vec{v}_1) \, T_o(12) >_2 (-n_o\Lambda^s)^{-1} \, \delta(t_5-t_4) \, v_{1x} >_1 \, . \qquad (III.49)$$

All matrix elements are known in their lowest non-vanishing order in q from (II.46) (III.12) and (III.41), and after performing all integrals we find for large times the result

$$\cdot \quad E_{(IA.1sss)}(t) = \frac{-D_o^2}{10\,\pi^{3/2}\,\beta m n_o\,(\nu_o+D_o)^{5/2}} \, t^{1/2} + O(1) \, . \qquad (III.50)$$

In order to obtain this expression we needed $(< \varphi^{s}_{\vec{q}} \, v_{1x} \, \varphi^{s}_{\vec{q}} >)^2$ as calculated in (III.41). Note that this square has a negative sign. Equation (III.50) is the only contribution to the dominant long time behaviour of the super Burnett coefficient involving the first correction term to the diffusive mode (II.37). The matrix elements in (III.49) need not be taken to higher order in q , since extra factors q in the q integral give rise to extra factors $t^{-1/2}$ in the result.

Next we estimate the contribution (fss) to the diagram IA.1 occurring in figure 9. In that case three δ functions of time are present and an extra factor q_x enters the q integral, coming from the matrix element $< \varphi^{s}_{\vec{q}}\, v_{1x}\, \varphi^{s}_{\vec{q}} >_1$ and therefore

$$\cdot \quad E_{(IA.1fss)}(t) \sim \int_0^t dt_1 \ldots \int_{t_4}^t dt_5\, \delta(t_1)\, \delta(t_2-t_1)\, h(t_4-t_1)\, \delta(t_5-t_4) \;,$$

where h(t) is some bounded function of time with a leading asymptotic behaviour smaller than t^{-2} for large t .

A straightforward estimate would lead to an asymptotic behaviour proportional to t^{-2} , but the coefficient of this term vanishes on performing the angular $\hat{q}$ integration.

Consequently

$$\cdot \quad E_{(IA.1fss)}(t) = O(1) \;. \tag{III.51}$$

The same arguments may be applied to the contribution (ssf) yielding the same result. The contributions (ffs) (fsf) (sff) and (fff) drawn in figure 9 involve at least four δ functions of time in the five-fold time integration given in (III.48) and are hence easily estimated to be finite for large t .

So we are left with the contribution (sfs) , which reads

$$\cdot \quad E_{(IA.1sfs)}(t) = \int_0^t dt_1 \ldots \int_{t_4}^t dt_5 \sum_{j=1,2} \int' d\vec{q}\, (2\pi)^{-3}\, n_o^{-1}$$

$$\exp\{-(\nu_o+D_o)q^2(t_4-t_1)\}\, \delta(t_1)\, \delta(t_3-t_2)\, \delta(t_5-t_4)$$

$$\left(< v_{1x}\, \varphi^{s}_{\vec{q}}(\vec{v}_1)\, \varphi^{\eta j}_{-\vec{q}}(\vec{v}_1) >_1 \right)^2 < \varphi^{s}_{\vec{q}}\, v_{1x}\, (1-P^{s}_{\vec{q}})\, (-n_o\Lambda^{s})^{-1}\, v_{1x}\, \varphi^{s}_{\vec{q}} >_1 \;.$$

The last matrix element equals D_o in the limit $q \to o$, as follows from (II.39), the other one is given in (III.12) and so we find

$$\cdot \quad E_{(IA.1sfs)}(t) = \frac{D_o}{6\,\pi^{3/2}\,\beta m n_o}\,\frac{1}{(D_o+\nu_o)^{3/2}}\, t^{1/2} + O(1) \;. \tag{III.52}$$

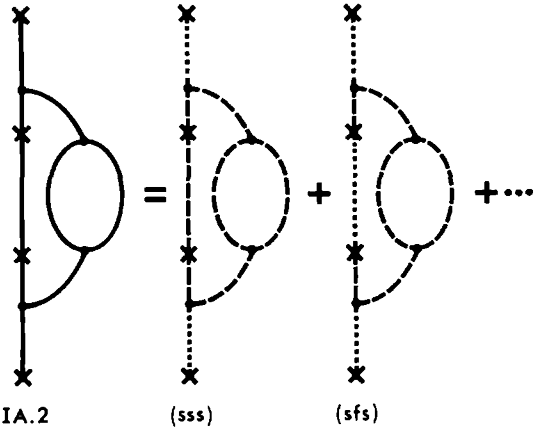


figure 10 : Decomposition of the diagram IA.2 belonging to subclass IA.

This contribution to $D^{(2)}(t)$ in (III.25a) cancels exactly the leading divergence in $E_3(t)$, as can be seen from the expression (III.25d) for $E_3(t)$.

So far we have studied completely the first diagram of class IA, drawn in figure 9 and we found two leading contributions to E(t) , which diverge as $t^{1/2}$.

Further diagrams of class IA can be obtained by replacing the Γ^s operators in (III.48) by ring propagators, R^s , according to figure 1. This will give no contributions to E(t) of orders, larger than log t . More important contributions are obtained from diagram 1A.2 drawn in figure 10.

The calculation of $E_{(IA.2sss)}(t)$, where in the side branch one shear mode, two opposite sound modes and one shear mode have to be taken from top to bottom, is rather lengthy but very similar to the calculation of $C^{(e)}(t)$ given in section a . To be more precise, the operator $T_{\vec{k}}(2,t)$ defined in (III.15) and given in (III.22) enters also in this calculation, as can be seen by comparing the diagrams e in figure 4 and (sss) in figure 10 .

Here we give only the result

$$E_{(IA.2sss)}(t) = -\frac{4}{15}\frac{D_o^2\,\Delta_\eta(1)\,\Gamma(15/4)}{\pi^2\,\beta m n_o\,(D_o+\nu_o)^{15/4}}\,t^{1/4} + O(1) . \quad \text{(III.53)}$$

The calculation of $E_{(IA.2sfs)}(t)$ yields a term proportional to $t^{1/4}$ cancelling in (III.25a) the contribution to $E_3(t)$ of order $t^{1/4}$, which originates from $C^{(e)}(t)$ (see III.25d).

All this is very similar to the treatment of diagram IA.1 in (III.48-52). Next contributions to diagram IA.2 are at most proportional to log t . One may continue, finding diagrams belonging to subclass IA, which give terms of order $t^{1/8}$, $t^{1/16}$, ... in the super Burnett coefficient.

Finally we consider the subclass I B drawn in figure 8. By the same straightforward estimation techniques and by first replacing all full propagators by their Boltzmann equivalents, one finds for the sum of all diagrams belonging to subclass IB at most a divergence like

$$E_{(IB)}(t) = \mathcal{O}((\log t)^2) \ . \qquad (III.54)$$

Similar estimates can be made for other subclasses of class I.

Summarizing we find that the super Burnett coefficient, $D^{(2)}(t)$, diverges as

$$D^{(2)}(t) = - \frac{D_o^2}{10\,\pi^{3/2}\,\beta m n_o\,(\nu_o+D_o)^{5/2}}\, t^{1/2} + - \frac{4}{15}\frac{D_o^2\,\Delta_\eta(1)\Gamma(15/4)}{\pi^2\,\beta m n_o\,(D_o+\nu_o)^{15/4}}\, t^{1/4} + \mathcal{O}(t^{1/8}) \ , \qquad (III.55)$$

as t approaches infinity.

The contributions to $D^{(2)}(t)$ arise from:
- diagrams belonging to subclass VA, (see III.34), yielding together a contribution $E_{(V.A)}(t)$, (see III.35), which cancels completely $E_1(t)$, (see III.25a,b);
- diagram IA.1sfs, (see III.52), which cancels the term proportional to $t^{1/2}$ in $E_3(t)$, (see III.25d);
- diagram IA.2sfs, which cancels the term proportional to $t^{1/4}$ in $E_3(t)$;
- diagram IA.1sss, (see III.50), which survives and gives the term proportional to $t^{1/2}$ in $D^{(2)}(t)$;
- diagram IA.2sss, (see III.53), which survives and gives the term proportional to $t^{1/4}$ in $D^{(2)}(t)$.

c. Discussion

Here we review briefly the results of this chapter, and consider the velocity correlation function first.

The expansion (III.1b) for $\widetilde{C}(t)$ (or equivalently the diagram expansion in figure 4) has the following properties:

- each term in (III.1b) (or each diagram in figure 4) has a unique density dependence if time is measured in units t_o , where t_o is on the order of the mean free time and inversely proportional to the density,
- only even powers in the density occur.

We note that these properties are valid only in the framework of the kinetic theory employed here, that is to say with the approximations (II.19) and (II.20), and with the q integrals restricted to $q < k_o$. This can be derived as follows.

If all times occurring in the weight of a diagram of figure 4 are measured in units t_o , then each time integral is replaced by

$$\cdot \quad \int_{t_1}^{t_2} dt' \; ... = n_o^{-1} \; (n_o t_o) \int_{t_1/t_o}^{t_2/t_o} d(t'/t_o) \; ...$$

and is therefore inversely proportional to the density.
We considered in this chapter wave numbers $\vec{q}$ such that $o \leqslant q \leqslant k_o$ where k_o was a cut-off wave number on the order of the inverse mean free path $k_o \sim l_o^{-1} \sim n_o \, \sigma^{d-1}$.
All wave vectors occurring in the weight of a diagram in figure 4 are scaled such that $\vec{q} = \vec{y} n_o$. Then each $\vec{q}$ integral is replaced by

$$\cdot \quad \int_{q<k_o} d\vec{q} \; ... = n_o^d \int_{y<y_o} d\vec{y} \; ...$$

and is therefore proportional to n_o^d (here d=3), since $y_o = k_o/n_o$ is density independent.

The operators $T_o(ij)$, $\Lambda^s(1)$, $\Lambda(i)$, acting on functions of the velocities, are independent of the density as is clear from (II.21) and (II.32).

The Boltzmann propagators $\Gamma^s_{\vec{q}}(1,t)$ and $\Gamma_{\vec{q}}(i,t)$ are independent of the density if considered as functions of t/t_o and $\vec{y} = \vec{q}/n_o$ as follows from (II.30) and (II.31).

The diffusion mode $\varphi^s_{\vec{q}}(\vec{v}_1)$ (II.37) and the hydrodynamic modes $\varphi^j_{\vec{q}}(\vec{v}_i)$ (II.40,43,46) are independent of the density if considered as functions of $\vec{y}$ and $\vec{v}_1$ ($\vec{v}_i$ respectively). This follows from the way they were constructed in section II*c*, as normalized eigenfunctions of $L^s_{\vec{q}}(1)$ (II.31a) and $L_{\vec{q}}(i)$ (II.31b). The same property is valid for the projection operators $P^s_{\vec{q}}(1)$ and $P^j_{\vec{q}}(i)$ as defined by (II.51) and (II.52). As a consequence the quantities $z^s_q t$ and $z^j_q t$ considered as functions of y and t/t_o are independent of the density. Finally we note that the one particle average (II.2,3) is independent of the density too.

After this discussion of all quantities and operations which occur in the analytic expressions represented by the diagrams of figure 4, it is clear that the density dependence of a diagram is unique and can be obtained by counting the number of q integrals, t integrals and the number of particles involved (compare diagram rule 9 in section II*b*).

This can be done simply as follows.

In each diagram we call the number of vertices of type 1, 2 or 3 (see figure 2) N_1 , N_2 and N_3 respectively. It follows from diagram rule 2 that $N_1 = N_3$. The number of q integrals involved in the corresponding analytic expression of each diagram is $N_1 + N_2$, as can be seen from diagram rule 6. Except for particle 1 , the number of particles occurring in a diagram is equal to N_1 , as follows from diagram rule 9.

The number of ordered time integrals is equal to the total number of vertices, $N_1 + N_2 + N_3$ (diagram rule 3). Therefore the density dependence of a diagram with N_1 , N_2 or N_3 vertices of type 1 , 2 or 3 respectively, is equal to

$$\cdot \quad [\, n_o^{d-1} \,]^{N_1 + N_2} \, . \tag{III.56}$$

which proves the second statement, made at the beginning of this section for d=3 .

In section *a* we investigated diagrams in the expansion of figure 4 for $\tilde{C}(t)$ and ordered them first with respect to their dominant long time behaviour. In this way we found a set of contributions, which were short ranged in time (e.g. (III.4) and (III.11b)). Of all these terms the Boltzmann contributions $\tilde{C}^{(B)}(t)$ (III.4,5) is the dominant one in the density. According to figure 4 and relation (III.56) it is proportional to n_o^o , and there are no other contributions of this order.
We found a set of diagrams (e.g. 4b,4c,4d) with an asymptotic time behaviour proportional to $(t_o/t)^{3/2}$. Of these terms the ring contribution $\tilde{C}^{(R)}(t)$ (III.13) is the dominant one since it is proportional to n_o^2 , according to (III.56).
In fact the diagram expansion of figure 4 considered in section *a* yields an expression for $\tilde{C}(t)$ of the structure

$$\begin{aligned}
\cdot \quad \tilde{C}(t) = \delta(t/t_o)\, & [\ \mathcal{O}(n_o^o) + \mathcal{O}(n_o^2) + \dots\ ] \\
& + (t_o/t)^{3/2}\, [\ \mathcal{O}(n_o^2) + \mathcal{O}(n_o^4) + \dots\ ] \\
& + (t_o/t)^{7/4}\, [\ \mathcal{O}(n_o^4) + \mathcal{O}(n_o^6) + \dots\ ] \\
& + (t_o/t)^{15/8}\, [\ \mathcal{O}(n_o^6) + \mathcal{O}(n_o^8) + \dots\ ] \\
& + \dots
\end{aligned}$$

$$+ (t_o/t)^2 [\ \mathcal{O}(n_o^2) + \mathcal{O}(n_o^4) + \ldots\ ]$$

$$+ \ldots \tag{III.57}$$

and we have calculated explicitly the coefficients of the first three terms in this expansion to lowest non-vanishing order in the density, compare (III.24a).

According to (III.56) the term of order n_o^o in this expansion arises from diagram 4a, *all* terms of order n_o^2 arise from the ring diagram 4b, and so on.

It may be possible that there are contributions to $\tilde{C}(t)$, which are of type $(t_o/t)^2 \log(t/t_o)$ in time. If this is indeed the case they are at least of order n_o^6 in the density.

As discussed in section II*a*, the coefficients of the terms $\delta(t/t_o)$, $(t_o/t)^{3/2}$, $(t_o/t)^{7/4}$, ..., $(t_o/t)^{2-2^{-m}}$ in (III.57) are predicted correctly from the approximate kinetic theory, to lowest non-vanishing order in the density.

On the basis of our approximate kinetic theory one could calculate higher density corrections to these results or calculate the coefficients of terms like $(t_o/t)^{2+\epsilon}$ $(\epsilon \geq o)$, however such predictions can not be trusted a priori, as will be discussed below.

At this point we make some further remarks about the approximations (II.19) and (II.20).

It is very well possible to drop these approximations and to study a kinetic theory, which contains the full binary collision operator T(ij) defined in (II.8) and all statistical correlations as appear in (II.18). The first effect will be that in the diagrams to be considered a wave number dependent collision operator $T_{\vec{k}}(ij)$ appears, instead of $T_o(ij)$, which is the Fourier transform of T(ij) and given by

$$T_{\vec{k}}(ij) = \sigma^{d-1} \int_{\vec{v}_{ij}\cdot\hat{\sigma}<o} d\hat{\sigma}\ |\ \vec{v}_{ij}\cdot\hat{\sigma}\ |\ \exp(-i\vec{k}\cdot\sigma\hat{\sigma})\ \{\ b_{\hat{\sigma}}(ij)-1\ \}\ . \tag{III.58}$$

By expanding this operator in powers of k we obtain

$$\cdot \quad T_{\vec{k}}(ij) = T_o(ij) + n_o\, \mathcal{O}(k/n_o) \;, \qquad \text{(III.59)}$$

where k/n_o is a scaled wave number. The term $n_o\, \mathcal{O}(k/n_o)$ in this expression gives corrections to the velocity correlation function, which are of order $n_o\, f(t/t_o)$ relative to the dominant contributions in (III.57), which are of type $(t_o/t)^{2-2^{-m}}\, \mathcal{O}(n_o^{2m})$ $(m=1,2,3,\dots)$. Here $f(t/t_o)$ is some bounded function with an asymptotic time behaviour at most proportional to $(t_o/t)^{1/2}$. This is due to the fact that an extra factor k in the integrals considered in section *a* gives rise to an extra factor $t^{-1/2}$ in the result. Therefore the approximate kinetic theory is a priori restricted to phenomena, which are larger than $\mathcal{O}(t^{-1/2})$ relative to the dominant long time behaviour (here $t^{-3/2}$) . From the more precise arguments presented above it is also clear that terms in (III.57) of type $(t_o/t)^2$ are to order n_o^2 , completely determined by the ring event (calculated by means of the approximate kinetic theory), however its coefficient vanishes by symmetry.
In addition we note that diagrams like 4c,4d,4e,... give apart from the term calculated in (III.14-23) contributions to $\tilde{C}(t)$ of the form $(t_o/t)^2\, n_o^4$. The coefficient seems to be non-vanishing.

Secondly we mention that statistical correlations (which are left out in the approximate kinetic theory according to (II.19)) should yield higher order density corrections in the expression (III.57), which do not affect the coefficients to lowest non-vanishing order in the density and do not introduce terms with an asymptotic time behaviour not yet contained in that expansion.

Finally we discuss the approximation, which is made by introducing cut-off wave numbers (k_o) in all q integrals occurring in this chapter.

In the complete and systematic theory, integrals over wave vectors ($\vec{q}$) extend over all values of q , so that $o \leqslant q < \infty$.
In the approximate kinetic theory one has to introduce a cut off wave number on the order of the inverse correlation length (σ^{-1}) , such that $o \leqslant q \leqslant \sigma^{-1}$. This is due to the fact that the approximations (II.19) and (II.20) are obviously wrong for distances smaller than the hard sphere diameter σ (or for wave vectors larger than σ^{-1}).
To derive the long time behaviour of the various contributions to $\tilde{C}(t)$, in the expansion (III.1b), it was sufficient to consider wave numbers q in the region $o \leqslant q \leqslant k_o$ only. Note that for low densities $k_o < \sigma^{-1}$, since $k_o \sim n_o \sigma^{d-1}$. To illustrate the error made by doing so we consider that part of the ring contribution $\tilde{C}^{(R)}(t)$ in (III.8), which arises from values of q , in the q integral of (II.34), in the region $k_o \leqslant q \leqslant \sigma^{-1}$.
We start from the expression

$$\tilde{C}^{(R)}_{(>)}(t) = n_o \, (2\pi)^{-d} \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{k_o \leqslant q \leqslant \sigma^{-1}} d\vec{q}$$

$$< < v_{1x} \, \Gamma_o^s(1,t_1) \, T_o(12) \, \Gamma^s_{-\vec{q}}(1,t_2-t_1) \, \Gamma_{\vec{q}}(2,t_2-t_1)$$

$$T_o(12) \, \Gamma_o^s(1,t-t_2) \, v_{1x} >_1 >_2 \, , \tag{III.60}$$

where the Boltzmann propagators $\Gamma^s_{-\vec{q}}$ and $\Gamma_{\vec{q}}$ are defined in (II.30-32). The decompositions (II.50a) and (II.50b) into slowly and fastly parts are meaningless for $q \geqslant k_o$. We therefore consider the Laplace transform $C^{(R)}_{(>)}(z)$ of (III.60) and notice that it is an analytic function in the half plane Re $z > - a \, t_o^{-1} \sim n_o$ (a real and positive). Therefore $\tilde{C}^{(R)}_{(>)}(t)$ is proportional to $\exp(-t/t_o)$ and can be replaced by a properly normalized δ function in time

$$\cdot \quad \tilde{C}^{(R)}_{(>)}(t) = C^{(R)}_{(>)}(o)\ \delta(t) = C^{(R)}_{(>)}(o)\ t_o^{-1}\ \delta(t/t_o)\ . \tag{III.61}$$

Defining the scaled wave number $\vec{y}$ as $\vec{y} = \vec{q}/n_o$, we find for the coefficient in (III.61)

$$\cdot \quad C^{(R)}_{(>)}(o) = -\ (2\pi)^{-d}\ n_o^{d-2} \int\limits_{\sigma^{d-1}\leq y\leq 1/(n_o\sigma)} d\vec{y}$$

$$< < v_{1x}\ (\Lambda^s)^{-1}\ T_o(12)\ \frac{1}{i\vec{y}.\vec{v}_{12} + \Lambda^s + \Lambda(2)}\ T_o(12)\ (\Lambda^s)^{-1}\ v_{1x} >_1 >_2\ . \tag{III.62}$$

The density dependence of this expression is obtained from the behaviour of the integrand for large values of y . Explicit calculations indicate that the integrand is proportional to $y^{-2} + y^{-3} + \ldots$. One would expect a dominant behaviour proportional to y^{-1} however the coefficient vanishes due to the property

$$\cdot \quad \ldots\ T_o(12)\ \frac{1}{i\vec{y}.\vec{v}_{12}}\ T_o(12)\ \ldots = o\ .$$

This follows from the geometrical consideration that two particles can never collide twice in the absence of an interaction with a third particle. From this argument follows that

$$\cdot \quad C^{(R)}_{(>)}(o) \sim n_o^{d-2} \int\limits_{\sigma^{d-1}}^{1/(n_o\sigma)} dy\ y^{d-1}\ \{ \frac{a}{y^2} + \frac{b}{y^3} + \ldots \}\ ,$$

which yields the final estimate for $\tilde{C}^{(R)}_{(>)}(t)$

$$\cdot \quad \tilde{C}^{(R)}_{(>)}(t) = \delta(t/t_o)\ [\ \mathcal{O}(n_o) + \mathcal{O}(n_o^2 \log n_o) + \ldots\ ] \quad (d=3) \tag{III.63}$$

$$\cdot \quad \tilde{C}^{(R)}_{(>)}(t) = \delta(t/t_o)\ [\ \mathcal{O}(n_o \log n_o) + \ldots\ ]\ . \quad (d=2) \tag{III.64}$$

The conclusion is that the ring event contains contributions to $\tilde{C}(t)$, which are short ranged in time and non-analytic in the density.
We note here that the contributions (III.63,64) give terms in the Navier Stokes self diffusion coefficient D, as defined by (I.70), which are non-analytic in the density. These terms are extensively discussed in references (Kawasaki 1964; Haines 1966; Weyland 1967; Cohen 1967).

Summarizing we notice that all three sources of higher density corrections mentioned above introduce in (III.57) terms in the existing coefficients, which are odd in n or even non-analytic.

The result (III.57) for $\tilde{C}(t)$, obtained from the low density kinetic theory, yields for the time dependent diffusion coefficient $D^{(o)}(t)$ according to (I.45)

$$
\begin{aligned}
D^{(o)}(t) = {} & [\, \mathcal{O}(n_o^{-1}) + \mathcal{O}(n_o^{-3}) + \dots \,] + \\
& + (t_o/t)^{1/2} [\, \mathcal{O}(n_o^{-3}) + \mathcal{O}(n_o^{-5}) + \dots \,] + \\
& + (t_o/t)^{3/4} [\, \mathcal{O}(n_o^{-5}) + \mathcal{O}(n_o^{-7}) + \dots \,] + \\
& + \dots + t_o/t\, [\, \mathcal{O}(n_o^{-3}) + \dots \,] \, ,
\end{aligned}
\qquad \text{(III.65)}
$$

where the coefficients of the first three terms to lowest non-vanishing order in the density are given by (III.24b).

Finally in this section we consider the time dependent super Burnett coefficient $D^{(2)}(t)$.
The diagrams contributing to $D^{(2)}(t)$ (or rather E(t)) mentioned in figure 5,6,8,9,10 have a unique density dependence (if time is measured in units t_o) given by

$$\cdot \quad n_o^{-3} [n_o^{d-1}]^{N_1+N_2} , \tag{III.66}$$

where N_1 and N_2 are the number of vertices of type 1 and 2 occurring in a diagram. The derivation of (III.66) is similar to that of (III.56) for $\tilde{C}(t)$ and will be omitted.

We have found in section *b* a series expansion for $D^{(2)}(t)$ of the structure

$$\begin{aligned} \cdot \quad D^{(2)}(t) = [\mathcal{O}(n_o^{-3}) + \mathcal{O}(n_o^{-1}) + \dots] &+ \\ + (t/t_o)^{1/2} [\mathcal{O}(n_o^{-1}) + \mathcal{O}(n_o) + \dots] &+ \\ + (t/t_o)^{1/4} [\mathcal{O}(n_o) + \mathcal{O}(n_o^{3}) + \dots] &+ \dots , \end{aligned} \tag{III.67}$$

where the coefficients of the first three terms were calculated explicitly to lowest non-vanishing order in the density, compare (III.37b) and (III.55).

CHAPTER IV

Kinetic theory calculations in two dimensions

a. The velocity correlation function

In this chapter we apply the kinetic theory of hard spheres at low densities, given in chapter II, to the calculation of the velocity correlation function and the time dependent super Burnett coefficient in two dimensional systems.

The actual calculations proceed along the same lines as in the three dimensional case but the diagrams are ordered in a different way.

In chapter III (d=3) we ordered the diagrams first with respect to their dominant long time behaviour. In this way we found for the diffusion coefficient $D^{(o)}(t)$ and the super Burnett coefficient $D^{(2)}(t)$ series expansions of the type (III.65) and (III.67) where each term is *less* important in time than the previous one, as $t \to \infty$. The same procedure could be applied for the two dimensional case too. Then one would find a series of more and more complicated diagrams, which are of increasingly higher order in the density giving contributions to $D^{(o)}(t)$ and $D^{(2)}(t)$, which are increasingly *more* divergent as t tends to infinity.

Therefore it is more convenient to reverse the ordering procedure for diagrams in the two dimensional case.

In this chapter we first collect diagrams, which are of the same order in the density, where time is measured in units t_o (t_o is proportional to n_o^{-1} as discussed in chapter II). Then we study within such a set the behaviour of the diagrams for large values of t/t_o . In each order in the density each *new* type of asymptotic time behaviour (which was not present in the previous order), is predicted correctly by our low density kinetic theory, according to the discussions in section II*a*.

In two dimensions we will find that each new type of asymptotic time

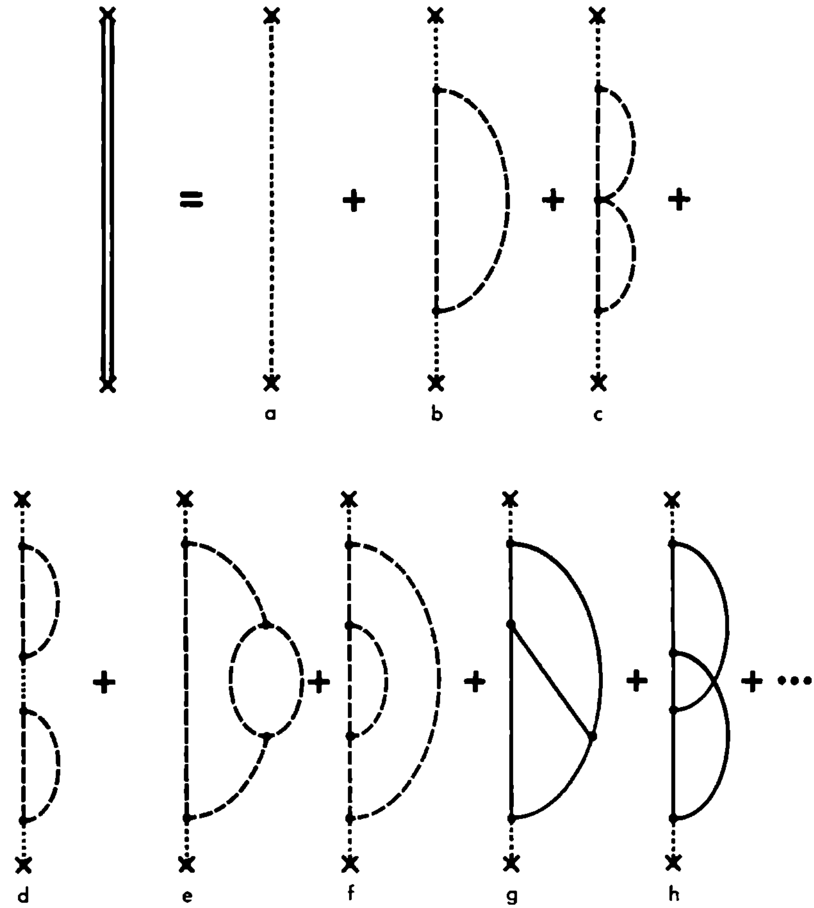


figure 11 : Various contributions to the velocity correlation function for a two dimensional system.

behaviour is *more* divergent in time than the dominant behaviour in the previous order in the density; for d=3 each new type of asymptotic time behaviour was *less* divergent than the dominant behaviour in the previous order in the density (compare (III.65) and (III.67)).

This section is devoted to a calculation of $D^{(o)}(t)$ and the velocity correlation function.
We start with the velocity correlation function $\tilde{C}(t)$, given in (II.6), and use the diagrammatic representation given in figure 11 (cfr. (III.1) and figure 4)

$$\tilde{C}(t) = \tilde{C}^{(B)}(t) + \tilde{C}^{(R)}(t) + \tilde{C}^{(c)}(t) + \tilde{C}^{(d)}(t) + \ldots , \qquad \text{(IV.1)}$$

where all contributions have to be calculated for d=2 .
Using the fact that

$$P_o^S(1) \mid v_{1x} > = o \; ; \; < v_{1x} \mid P_o^S(1) = o \qquad \text{(IV.2)}$$

it is seen directly that all diagrams on the right hand side of figure 11 start and end with the fastly decaying part of the Boltzmann self propagator as indicated.
If time is measured in units t_o , where $t_o \sim n_o^{-1}$, each diagram in figure 11 (or equivalently each term in (IV.1)) has a unique density dependence given by

$$n_o^{\;N_1 + N_2} . \qquad \text{(IV.3)}$$

Here N_1 and N_2 are the number of vertices of type 1 and 2 respectively occurring in a diagram (see figure 2). The proof of this statement is given in (III.56).
According to (IV.3) and figure 11, the Boltzmann contribution $\tilde{C}^{(B)}(t)$ is of zeroth order in the density, the ring contribution $\tilde{C}^{(R)}(t)$ is

proportional to n_o , the set of diagrams c - h is of order n_o^2 , all further diagrams in figure 11 are at least proportional to n_o^3 .

The Boltzmann contribution is explicitly given by (cfr. (III.3))

$$\tilde{C}^{(B)}(t) = \langle v_{1x}\, \Gamma_o^s(1,t)\, v_{1x} \rangle_1 = \langle v_{1x} \exp(n_o \Lambda^s t)\, v_{1x} \rangle_1 \;. \qquad (IV.4)$$

In first Enskog approximation this expression yields (cfr. (III.5-7))

$$\tilde{C}^{(B)}(t) = (\beta m)^{-1} \exp(-t/t_o) \;, \qquad (IV.5)$$

where t_o is the low density value of the mean free time (Dorfman 1972)

$$t_o = \frac{(\beta m/\pi)^{1/2}}{4 n_o \sigma} \;. \qquad (IV.6)$$

Since the Boltzmann value of the self diffusion coefficient $D_o = \int_0^\infty dt\, \tilde{C}^{(B)}(t)$, we can obtain its first Enskog approximation $[D_o]_1$ from (IV.5) by integrating over time

$$[D_o]_1 = (\beta m)^{-1}\, t_o \;. \qquad (IV.7)$$

It is equal to D_o within a few percent. This can be seen by calculating the second Enskog approximation to D_o yielding

$$[D_o]_2 = [D_o]_1 \left(1 - (16d+11)^{-1} \right)^{-1} \;, \qquad (IV.8)$$

where d is the dimensionality (here d=2).
For d=3 this expression coincides with the result given in ref. (Chapman 1960). Since we are interested in long times it will be sufficient for our purposes to represent $\tilde{C}^{(B)}(t)$, which is short ranged in time, by a properly normalized δ function. From (IV.4) and the definition for the Boltzmann value of the self diffusion coefficient (II.39) follows

that

$$\cdot \quad \tilde{C}^{(B)}(t) = D_o/t_o\ \delta(t/t_o) = D_o\ \delta(t) \ . \tag{IV.9}$$

Next we consider the ring contribution $\tilde{C}^{(R)}(t)$ and start from the definition (cfr. (III.8))

$$\cdot \quad \tilde{C}^{(R)}(t) = \langle v_{1x}\ R_o^s(1,t)\ v_{1x} \rangle_1 \ , \tag{IV.10}$$

where the ring propagator is given in (II.34), so that

$$\cdot \quad \tilde{C}^{(R)}(t) = n_o \int_o^t dt_1 \int_{t_1}^t dt_2 \int d\vec{q}\ (2\pi)^{-2}$$

$$\langle \langle v_{1x}\ \Gamma_o^s(t_1)\ T_o(12)\ \Gamma_{-\vec{q}}^s(t_2-t_1)\ \Gamma_{\vec{q}}(2,t_2-t_1)\ T_o(12)\ \Gamma_o^s(t-t_2)\ v_{1x} \rangle_1 \rangle_2 \tag{IV.11}$$

and we have written shortly $\Gamma_{\vec{q}}^s(t)$ for $\Gamma_{\vec{q}}^s(1,t)$.
We will not consider the short time behaviour of $\tilde{C}^{(R)}(t)$ since in this order in the density (n_o) such contributions to $\tilde{C}(t)$ are not predicted correctly from the kinetic theory used here, as was discussed in sections II*a* and III*c*.
From property (IV.2) it follows that only the fastly decaying parts of $\Gamma_o^s(t_1)$ and $\Gamma_o^s(t-t_2)$ in (IV.11) contribute.
The long time behaviour of $\tilde{C}^{(R)}(t)$ is obtained by replacing the intermediate Boltzmann propagators in (IV.11) by their slowly decaying parts as is indicated in diagram 11b.
Then we find from (II.50-54) after performing the integrals over t_1 and t_2 in (IV.11)

$$\cdot \quad \tilde{C}^{(R)}(t) = n_o^{-1}\ (2\pi)^{-2} \sum_{j=1}^{4} \int' d\vec{q}\ \exp\{(z_q^j+z_q^s)t\} \tag{IV.12}$$

$$\langle v_{1x}\ (\Lambda^s)^{-1} \langle T_o(12)\ P_{-\vec{q}}^s(1)\ P_{\vec{q}}^j(2)\ T_o(12) \rangle_2\ (\Lambda^s)^{-1}\ v_{1x} \rangle_1 \ .$$

The prime on the integral sign indicates that $q < k_o$ where k_o is a cut-off wave number of the order of the inverse mean free path $k_o \sim l_o^{-1} \sim n_o \sigma$.

Here we quote a result, discussed already in section IIIc, which is useful in estimating the density and time dependence of expressions like (IV.12), namely:

- The quantites $\varphi^s_{\vec{q}}(\vec{v}_1)$, $\varphi^j_{\vec{q}}(\vec{v}_2)$, $P^s_{\vec{q}}(1)$, $P^j_{\vec{q}}(2)$, $\Gamma^s_{\vec{q}}(t)$, $\Gamma_{\vec{q}}(2,t)$, $z^s_q t$ and $z^j_q t$ are independent of the density if they are considered as functions of $\vec{q}/n_o$ and t/t_o ,

Consequently the self diffusion mode and the hydrodynamic modes with corresponding frequencies have the following structure (compare II.37-47))

$$\cdot \quad \varphi^s_{\vec{q}} \sim \varphi^j_{\vec{q}} \sim O(1) + O(i\vec{q}/n_o) + O((q/n_o)^2) + \dots \tag{IV.13}$$

$$\cdot \quad z^s_q \sim z^j_q \sim n_o \,[\, O((q/n_o)^2) + O((q/n_o)^4) + \dots \,] \qquad (j \neq \sigma)$$

$$\cdot \quad z^\sigma_q \sim n_o \,[\, O(iq/n_o) + O((q/n_o)^2) + \dots \,] \; . \tag{IV.14}$$

The coefficients D_o , ν_o , D_{To} , Γ_{so} occurring in the expressions for the frequencies z^s_q , z^j_q are of the same order of magnitude and inversely proportional to the density.

To calculate (IV.12) we first take the self diffusion mode and the hydrodynamic modes involved in the projection operators $P^s_{\vec{q}}$ and $P^j_{\vec{q}}$ in zeroth order in q . Afterwards the higher order terms in (IV.13) are considered. By applying the property (II.57) the operators Λ^s and $T_o(12)$ in (IV.12) can be eliminated, yielding

$$\cdot \quad \tilde{C}^{(R)}(t) = n_o^{-1} \, (2\pi)^{-2} \sum_{j=1}^{4} \int' d\vec{q}$$

$$\{ < v_{1x} \, \varphi^{j}_{\vec{q}}(\vec{v}_1) \, \varphi^{s}_{-\vec{q}}(\vec{v}_1) >_1 \}^2 \exp \{ (z^j_q + z^s_q) t \} \, , \tag{IV.15}$$

which is the analogue of (III.10). Notice that there is only one shear mode for d=2 .
The shear mode contribution to $\tilde{C}^{(R)}(t)$ ($j=\eta$ in (IV.15)) can be obtained by calculating the corresponding matrix element to lowest order in q from (II.37) and (II.46), yielding

$$\cdot \quad \{ < v_{1x} \, \varphi^{\eta}_{\vec{q}} \, \varphi^{s}_{-\vec{q}} >_1 \}^2 = (\beta m)^{-1} \, (1-\hat{q}_x^2) \; . \tag{IV.16}$$

Therefore the shear mode contribution in (IV.15) has the structure

$$\cdot \quad \tilde{C}^{(R)}_{(\eta)}(t) \sim n_o^{-1} \int_o^{k_o} dq \; q \; \exp(-D' q^2 t) \; . \tag{IV.17}$$

Here and in the following estimates D' stands for a typical diffusivity (or combination therefore), such as D_o , ν_o , D_{To} or Γ_{so} .
For $t \gg t_o$ the upper limit on the q integral may be replaced by infinity, yielding

$$\cdot \quad \tilde{C}^{(R)}_{(\eta)}(t) \sim n_o \; t_o/t \; . \tag{IV.18}$$

Explicit calculation yields from (IV.15) and (IV.16)

$$\cdot \quad \tilde{C}^{(R)}_{(\eta)}(t) = (d_o/t_o) \; (t_o/t) \; , \tag{IV.19}$$

where the coefficient d_o is given by

$$\cdot \quad d_o = \frac{1}{8\pi \, \beta m n_o (D_o + \nu_o)} \tag{IV.20}$$

and is of zeroth order in the density.

The matrix elements in (IV.15) corresponding to the sound mode contributions are equal to

$$\cdot \quad \{ < v_{1x}\, \varphi^{\sigma}_{\vec{q}}\, \varphi^{s}_{-\vec{q}} >_1 \}^2 = (2\beta m)^{-1}\, \hat{q}_x^2 \ . \tag{IV.21}$$

Therefore the contributions of the two sound modes together may be estimated as

$$\cdot \quad \tilde{C}^{(R)}_{(+,-)}(t) \sim n_o^{-1} \int_o^{k_o} dq\, q\, \cos(c_o qt)\, \exp(-D'q^2t) \tag{IV.22}$$

and we find straightforwardly for $t >> t_o$

$$\cdot \quad \tilde{C}^{(R)}_{(+,-)}(t) \sim n_o\, (t_o/t)^2 \ . \tag{IV.23}$$

We note here that the extra factor $\cos(c_o qt)$ in (IV.22) compared to (IV.17) gives an extra factor t_o/t in the result (IV.23) compared to (IV.18). This observation will be useful in the estimating procedure in this chapter. The heat mode in (IV.15) does not contribute if the modes are taken to zeroth order in q , since the amplitude vanishes

$$\cdot \quad < v_{1x}\, \varphi^{T}_{\vec{q}}\, \varphi^{s}_{-\vec{q}} >_1 = o \ . \tag{IV.24}$$

Finally we consider the self diffusion mode and the hydrodynamic modes involved in (IV.12) to first order in q . The terms of order q in these expressions give corrections to the above results. For $j=\eta$ and $j=T$ in (IV.12) these corrections are of the form

$$\cdot \quad n_o^{-1} \int_o^{k_o} dq\, q\, (q/n_o)^2\, \exp(-D'q^2t) \tag{IV.25}$$

and therefore they are proportional to

$$\cdot \quad \sim n_o \, (t_o/t)^2 \; . \tag{IV.26}$$

Note that the extra factor $(q/n_o)^2$ in (IV.25) compared to (IV.17) gives an extra factor t_o/t in the result, which again is a useful property in this chapter to estimate contributions to $\tilde{C}(t)$.
From the same observation it is easy to see that the correction terms to the sound modes in (IV.12) give contributions to $\tilde{C}^{(R)}(t)$, which are still smaller than (IV.23).
Summarizing we find from (IV.19-26) for the ring contribution to $\tilde{C}(t)$

$$\cdot \quad \tilde{C}^{(R)}(t) = d_o/t_o \, [\; t_o/t + \mathcal{O}((t_o/t)^2) \;] \; , \tag{IV.27}$$

which is the well-known long time tail in the velocity correlation function for two dimensional systems (Dorfman 1970). The coefficient d_o is given in (IV.20). It will be convenient to study further contributions to $\tilde{C}(t)$ in Laplace language. For comparison we give the Laplace transform of $\tilde{C}^{(R)}(t)$

$$\cdot \quad C^{(R)}(z) = d_o \; \{ \; \log(z_o/z) + \mathcal{O}(1) \; \} \; , \tag{IV.28}$$

where $z \ll z_o$ and z_o is of the order of the inverse mean free time t_o^{-1} .
We note that the long time behaviour of $\tilde{C}^{(R)}(t)$ reflects itself in a non-analytic behaviour of $C^{(R)}(z)$ for $z \to o$.

To obtain the contributions to $\tilde{C}(t)$ to the next order in the density we have collected in figure 11 the set of diagrams (c-h) which are of order n_o^2 according to the relation (IV.3).
We will show that the dominant singularities to this order in the density are of a new type, namely

$$\cdot \quad \sim n_o \, (\log(z_o/z))^2$$

for small z in Laplace language, or

$$\cdot \quad \sim n_o^2 \, (t_o/t) \, \log(t/t_o)$$

for large times in time language.
We will also find singularities of the form $n_o \log(z_o/z)$, which are higher density corrections to (IV.28). They should be neglected consistently in this low density kinetic theory.

By a calculation similar to that of the ring contribution $\tilde{C}^{(R)}(t)$ given above, one can show that the contribution of the upper ring in diagram 11c is proportional to $(t_2-t_1)^{-1}$ if $t_2-t_1 \gg t_o$ and the lower ring contribution is proportional to $(t_3-t_2)^{-1}$ for $t_3-t_2 \gg t_o$. By performing the time ordered integrations one finds

$$\cdot \quad \tilde{C}^{(c)}(t) \sim n_o^2 \, [\; t_o/t \, \log(t/t_o) + O(t_o/t) \;] \tag{IV.29}$$

and simularly for diagram 11d

$$\cdot \quad \tilde{C}^{(d)}(t) \sim n_o^2 \, [\; t_o/t \, \log(t/t_o) + O(t_o/t) \;] \; . \tag{IV.30}$$

Note that these contributions to $\tilde{C}(t)$ are more dominant in time than the ring contribution $\tilde{C}^{(R)}(t)$.
The explicit analytic expression for $\tilde{C}^{(c)}(t)$ contains a factor of the form

$$\cdot \quad \ldots < < \varphi^{s}_{-\vec{q}}(\vec{v}_1) \, \varphi^{j}_{\vec{q}}(\vec{v}_2) \, T_o(12) \, \varphi^{s}_{-\vec{k}}(\vec{v}_1) \, \varphi^{m}_{\vec{k}}(\vec{v}_2) >_1 >_2 \ldots \, . \tag{IV.31}$$

The expression for $\tilde{C}^{(d)}(t)$ contains a factor

$$\cdot \quad \int_{t_2}^{t_3} dt_2' < < \varphi^s_{-\vec{q}}(\vec{v}_1)\ \varphi^j_{\vec{q}}(\vec{v}_2)\ T_o(12) >_2 (-n_o\Lambda^s)^{-1}$$

$$\delta(t_2'-t_2)\ n_o < T_o(13)\ \varphi^s_{-\vec{k}}(\vec{v}_1)\ \varphi^m_{\vec{k}}(\vec{v}_3) >_3 >_1 \dots \quad \text{(IV.32)}$$

Otherwise both analytic expressions for $\tilde{C}^{(c)}(t)$ and $\tilde{C}^{(d)}(t)$ are the same. The dominant long time behaviour of $\tilde{C}^{(c)}(t)$ and $\tilde{C}^{(d)}(t)$, as estimated in (IV 29,30) is obtained from their explicit analytic expressions by taking all modes in zeroth order in q, similarly to the calculation of $\tilde{C}^{(R)}(t)$ given above. Then the property (II.57) may be applied to (IV.32) and one finds that both factors (IV.31) and (IV.32) are each others opposite. Therefore the dominant long time behaviour of $\tilde{C}^{(c)}(t)$ and $\tilde{C}^{(d)}(t)$ cancel and we conclude

$$\cdot \quad \tilde{C}^{(c)}(t) + \tilde{C}^{(d)}(t) \sim n_o^2\ O(t_o/t)\ , \quad \text{(IV.33)}$$

which is our final result for the diagrams 11c and 11d.

Next we consider the contribution $\tilde{C}^{(e)}(t)$ arising from diagram 11e and reading explicitly (cfr. III.14)

$$\cdot \quad \tilde{C}^{(e)}(t) = n_o^{-1}\ (2\pi)^{-2} \int' d\vec{q}\ \exp(z_q^s t)$$

$$< v_{1x}\ (\Lambda^s)^{-1} < T_o(12)\ P^s_{-\vec{q}}(1)\ \Upsilon_{\vec{q}}(2,t)\ T_o(12) >_2 (\Lambda^s)^{-1}\ v_{1x} >_1 ,$$

(IV.34)

where the operator $\Upsilon_{\vec{q}}(2,t)$ stands for the side branch of diagram 11e so that

$$\cdot \quad \Upsilon_{\vec{q}}(2,t) = n_o \int_o^t dt_1 \int_{t_1}^t dt_2\ (2\pi)^{-2} \int' d\vec{k}\ P_{\vec{q}}(2)\ \Gamma_{\vec{q}}(2,t_1)$$

$$< T_o(23)\ P_{\vec{k}}(2)\ \Gamma_{\vec{k}}(2,t_2-t_1)\ P_{\vec{l}}(3)\ \Gamma_{\vec{l}}(3,t_2-t_1)\ T_o(23)\ (1+P_{23}) >_3$$

$$P_{\vec{q}}(2)\ \Gamma_{\vec{q}}(2,t-t_2)\ , \qquad \text{(IV.35)}$$

where $\vec{l} = \vec{q}-\vec{k}$. Note that $\Upsilon_{\vec{q}}(2,t)$ starts and ends with a projection on a hydrodynamic mode since $P_{\vec{q}}(2) = \sum_j P^j_{\vec{q}}(2)$ with $j = T\ ,\ \sigma\ ,\ \eta$ according to (II.52).

Therefore the integrand of (IV.34) starts with a factor

$$\cdot \quad < v_{1x}\ (\Lambda^s)^{-1} < T_o(12)\ \varphi^s_{-\vec{q}}(\vec{v}_1)\ \varphi^j_{\vec{q}}(\vec{v}_2) >_1 >_2 \qquad \text{(IV.36)}$$

and it ends with

$$\cdot \quad < < \varphi^{j'}_{\vec{q}}(\vec{v}_2)\ \varphi^s_{-\vec{q}}(\vec{v}_1)\ T_o(12) >_2 (\Lambda^s)^{-1}\ v_{1x} >_1 \ . \qquad \text{(IV.37)}$$

These expressions are studied above (compare IV.12) and we have seen that they are of order q/n_o (IV.24) for $j=T$ or $j'=T$, and of order 1 (compare (IV.16) and (IV.21)) for $j=\sigma,\eta$ or $j'=\sigma,\eta$.

It turns out that the heat mode in (IV.36) or (IV.37) does not contribute to the leading long time behaviour of $\tilde{C}^{(e)}(t)$ since the integrand of (IV.34) contains at least one extra factor q/n_o compared to the case where $j=\eta$ in (IV.36) *and* $j'=\eta$ in (IV.37).

It can be shown explicitly that the sound modes in (IV.36) or (IV.37) do not contribute to the leading long time behaviour of $\tilde{C}^{(e)}(t)$ in (IV.34). The arguments use the fact that at least one extra factor $\cos(c_o q t_1)$ or $\cos(c_o q(t-t_2))$ enters the integrand of (IV.35) compared to the case where $j=\eta$ in (IV.36) and $j'=\eta$ in (IV.37). Such functions behave as extra damping factors in the q integral of (IV.34), equivalently to what we have seen in (IV.17) and (IV.22) for $\tilde{C}^{(R)}(t)$.

Summarizing it follows that only the shear mode in (IV.36) and (IV.37)

contributes to the leading long time behaviour of $\tilde{C}^{(e)}(t)$.
Therefore we replace the operator Υ in (IV.34) by its contribution

$$\cdot \quad \Upsilon_{\vec{q}}(2,t) = P_{\vec{q}}^{\eta}(2)\ \tilde{Y}(\vec{q},t)\ , \tag{IV.38}$$

where $\tilde{Y}(\vec{q},t)$ is given by

$$\cdot \quad \tilde{Y}(\vec{q},t) = < \tilde{\varphi}_{\vec{q}}^{\eta}(\vec{v}_2)\ |\ \Upsilon_{\vec{q}}(2,t)\ |\ \varphi_{\vec{q}}^{\eta}(\vec{v}_2)\ >_2\ . \tag{IV.39}$$

By calculating the expressions (IV.36) and (IV.37) for $j=\eta$ and $j'=\eta$ to lowest order in q one finds from (IV.16,34,38)

$$\cdot \quad \tilde{C}^{(e)}(t) = (\beta m n_o)^{-1}\ (2\pi)^{-2} \int' d\vec{q}\ (1-\hat{q}_x^2)\ e^{-D_o q^2 t}\ \tilde{Y}(\vec{q},t)\ . \tag{IV.40}$$

Its Laplace transform is given by

$$\cdot \quad C^{(e)}(z) = (\beta m n_o)^{-1}\ (2\pi)^{-2} \int' d\vec{q}\ (1-\hat{q}_x^2)\ Y(\vec{q},z+D_o q^2)\ , \tag{IV.41}$$

where $Y(\vec{q},z)$ is the Laplace transform of $\tilde{Y}(\vec{q},t)$.

In order to obtain the long time behaviour of $\tilde{C}^{(e)}(t)$ we study the non-analytic behaviour of $C^{(e)}(z)$ for $z \to o$.
An explicit expression for $Y(\vec{q},z)$ is obtained from (IV.35) and (IV.39) and reads (compare (III.15))

$$\cdot \quad Y(\vec{q},z) = \sum_{\lambda,\mu} Y^{\lambda\mu}(\vec{q},z) \tag{IV.42}$$

$$\cdot \quad Y^{\lambda\mu}(\vec{q},z) = \tfrac{1}{2}\ n_o\ (z+\nu_o q^2)^{-2}\ (2\pi)^{-2} \int' d\vec{k}\ (z-z_k^{\lambda}-z_l^{\mu})^{-1}\ M^{\lambda\mu}(\vec{k},\vec{l})\ , \tag{IV.43}$$

where λ,μ run over the hydrodynamic modes (T,σ,η) . The matrix element $M^{\lambda\mu}$ is given by

$$M^{\lambda\mu}(\vec{k},\vec{l}) = < \tilde{\varphi}^{\eta}_{\vec{q}}(\vec{v}_2) \mid < T_o(23)\ (1+P_{23})$$

$$P^{\lambda}_{\vec{k}}(2)\ P^{\mu}_{\vec{l}}(3)\ T_o(23)\ (1+P_{23}) >_3 \mid \varphi^{\eta}_{\vec{q}}(\vec{v}_2) >_2 . \qquad \text{(IV.44)}$$

The factor $\frac{1}{2}$ in front of (IV.43) and the first factor $(1+P_{23})$ in (IV.44) result from symmetrizing $M^{\lambda\mu}$ with respect to the variables $\vec{v}_2$ and $\vec{v}_3$.

The matrix element $M^{\lambda\mu}(\vec{k},\vec{l})$ vanishes for $\vec{q}=o$. This follows from (II.21) and the fact that the hydrodynamic modes $\varphi^{j}_{\vec{q}}(\vec{v}_2)$ in zeroth order in $\vec{q}$ are linear combinations of the summational invariants 1 , $\vec{v}_2$ and v_2^2 . Therefore the hydrodynamic modes at the beginning and at the end of (IV.44) are needed explicitly to *first* order in q . Here only the shear modes are needed, according to the previous discussion. One sees then from (IV.13) that this matrix element is at least proportional to

$$M^{\lambda\mu}(\vec{k},\vec{l}) \sim (q/n_o)^2 . \qquad \text{(IV.45)}$$

By taking the hydrodynamic modes involved in the projection operators $P^{\lambda}_{\vec{k}}(2)$ and $P^{\mu}_{\vec{l}}(3)$ in (IV.44), to *zeroth* order in k and l one finds from (II.46) and (II.58)

$$M^{\lambda\mu}(\vec{k},\vec{l}) = -\beta m\ (q/n_o)^2\ S^{\lambda\mu}_{\eta}(\vec{k},\vec{l}) \qquad \text{(IV.46)}$$

with

$$S^{\lambda\mu}_{\eta}(\vec{k},\vec{l}) = \{ < \varphi^{\lambda}_{\vec{k}}(\vec{v}_2)\ \varphi^{\mu}_{\vec{l}}(\vec{v}_2)\ (\hat{q}.\vec{v}_2)\ (\hat{q}_{\perp}.\vec{v}_2) >_2 \}^2 . \qquad \text{(IV.47)}$$

By taking the modes to *first* order in k or l one finds corrections to this result of relative order k or l . From the methods given below one can show that these correction terms will give no contributions to the leading long time behaviour of $\tilde{C}^{(e)}(t)$, but the details are omitted here.

The amplitudes in (IV.47) can be calculated from (II.40,43,46). We need explicitly

$$\cdot \quad S_{\eta}^{\eta\eta}(\vec{k},\vec{l}) = (\beta m)^{-2} \{ (\hat{q}_{\perp}.\hat{k}) (\hat{q}.\hat{l}) + (\hat{q}_{\perp}.\hat{l}) (\hat{q}.\hat{k}) \}^{2} \qquad \text{(IV.48a)}$$

$$\cdot \quad S_{\eta}^{TT}(\vec{k},\vec{l}) = S^{\eta T}(\vec{k},\vec{l}) = S^{T\eta}(\vec{k},\vec{l}) = 0 \qquad \text{(IV.48b)}$$

$$\cdot \quad S_{\eta}^{+-}(\vec{k},\vec{l}) = S_{\eta}^{-+}(\vec{k},\vec{l}) = (2\beta m)^{-2} \{ (\hat{q}.\hat{k}) (\hat{q}_{\perp}.\hat{l}) + (\hat{q}.\hat{l}) (\hat{q}_{\perp}.\hat{k}) \}^{2} . \qquad \text{(IV.48c)}$$

By means of (IV.43,46) the function $Y^{\lambda\mu}(\vec{q},z)$ can now be expressed as

$$\cdot \quad Y^{\lambda\mu}(\vec{q},z) = \frac{-\beta m}{8\pi^{2} n_{o}} \frac{q^{2}}{(z+\nu_{o} q^{2})^{2}} \int d\hat{k} \int_{o}^{k_{o}} dk\ k\ \frac{S_{\eta}^{\lambda\mu}(\vec{k},\vec{l})}{z-z_{k}^{\lambda}-z_{l}^{\mu}} . \qquad \text{(IV.49)}$$

In order to obtain the dominant non-analyticity of $C^{(e)}(z)$ from this expression and (IV.41) we apply the following method, which is described in detail in reference (Ernst 1974).

Take z positive real but arbitrarily small and introduce a quantity θ by

$$\cdot \quad \theta(q,z) = \max(q, \sqrt{z/(D_{o}+\nu_{o})}) , \qquad \text{(IV.50)}$$

which may be considered as a small parameter since the singularities of $C^{(e)}(z)$ for $z \to o$ arise from small values of q in the integrand of (IV.41). Then the function $Y^{\lambda\mu}(\vec{q},z)$ is divided into two parts

$$\cdot \quad Y^{\lambda\mu}(\vec{q},z) = Y_{(<)}^{\lambda\mu}(\vec{q},z) + Y_{(>)}^{\lambda\mu}(\vec{q},z) , \qquad \text{(IV.51)}$$

where the first term on the right hand side is obtained from (IV.49) by restricting the k integral to the interval $o < k < N_{o}\theta$, $(N_{o} > 1)$, the second term arises from values of k with $N_{o}\theta < k < k_{o}$.

The functions $Y^{\lambda\mu}_{(<)}$ are estimated in the following way. The amplitudes $S^{\lambda\mu}_{\eta}$ in (IV.49) are bounded from above as follows from (IV.48). The denominator in the integrand of (IV.49) is bounded from below by

$$\cdot \quad | z-z^{\lambda}_{k}-z^{\mu}_{l} | > | \mathrm{Re}(z-z^{\lambda}_{k}-z^{\mu}_{l}) | > z+D_{\lambda}k^2+D_{\mu}l^2 ,$$

where D_λ and D_μ are equal to ν_o , D_{To} or $\frac{1}{2}\Gamma_{so}$ according to the modes, which are taken into account. Since $\vec{l} = \vec{q}-\vec{k}$, we have for fixed $\vec{q}$ that

$$\cdot \quad D_\lambda k^2 + D_\mu l^2 \geq \frac{D_\lambda D_\mu}{D_\lambda + D_\mu} q^2$$

since the left hand side is a quadratic function of k . Therefore

$$\cdot \quad | z-z^{\lambda}_{k}-z^{\mu}_{l} | > D' \theta^2 , \tag{IV.52}$$

where D' is a typical diffusivity. From this follows that the function $Y^{\lambda\mu}_{(<)}$ is at most proportional to

$$\cdot \quad Y^{\lambda\mu}_{(<)}(\vec{q},z) \sim n_o^{-1} \frac{q^2}{(z+\nu_o q^2)^2} \int_o^{N_o\theta} dk\ k \frac{1}{D'\theta^2} .$$

Since $q \leq \theta$ and $z+\nu_o q^2 > D'\theta^2$ we find

$$\cdot \quad Y^{\lambda\mu}_{(<)}(\vec{q},z) \sim (n_o/\theta)^2 \tag{IV.53}$$

and its contribution to $C^{(e)}(z)$ denoted by $C^{(e)}_{(<)}(z)$, is at most proportional to

$$\cdot \quad C^{(e)}_{(<)}(z) \sim n_o \log(z_o/z) \tag{IV.54}$$

as follows directly by substituting (IV.53) in (IV.41).

Next we consider the function $Y^{\lambda\mu}_{(>)}(\vec{q},z)$, which is given by

$$Y^{\lambda\mu}_{(>)}(\vec{q},z) = \frac{-\beta m}{8\pi^2 n_o} \frac{q^2}{(z+\nu_o q^2)^2} \int d\hat{k} \int_{N_o\theta}^{k_o} dk\, k\, \frac{S^{\lambda\mu}_{\eta}(\vec{k},\vec{l})}{z-z^{\lambda}_{k}-z^{\mu}_{l}} . \qquad \text{(IV.55)}$$

Consider the difference

$$\left| \frac{1}{z-z^{\lambda}_{k}-z^{\mu}_{l}} - \frac{1}{-z^{\lambda}_{k}-z^{\mu}_{l}} \right| = \left| \frac{z}{(z-z^{\lambda}_{k}-z^{\mu}_{l})(z^{\lambda}_{k}+z^{\mu}_{l})} \right| < \theta^2/(D'k^4) \qquad \text{(IV.56)}$$

since the denominators satisfy the inequalities

$$| z-z^{\lambda}_{k}-z^{\mu}_{l} | > D'k^2 \qquad \text{(IV.57)}$$

$$| -z^{\lambda}_{k}-z^{\mu}_{l} | > D'k^2 . \qquad \text{(IV.58)}$$

Therefore the factor z in the denominator of the integrand of (IV.55) may be omitted, the error made by doing so is proportional to $(n_o/\theta)^2$ as can be seen from (IV.56).
Secondly the amplitudes $S^{\lambda\mu}_{\eta}(\vec{k},\vec{l})$ in (IV.55) can be replaced by $S^{\lambda\mu}_{\eta}(\vec{k},-\vec{k})$.
Since k is larger than q , the correction term is of order

$$S^{\lambda\mu}_{\eta}(\vec{k},\vec{l}) - S^{\lambda\mu}_{\eta}(\vec{k},-\vec{k}) = O(q/k) . \qquad \text{(IV.59)}$$

This follows from the property that $S^{\lambda\mu}_{\eta}(\vec{k},\vec{l})$ depends on $\vec{l}$ only through the combinations $\hat{q}.\vec{l}$ and $\hat{q}_{\perp}.\vec{l}$, which can be expanded in powers of q/k , the leading terms being $-\hat{q}.\hat{k}$ and $-\hat{q}_{\perp}.\hat{k}$ respectively. The term of order q/k in (IV.59) yields in (IV.55) corrections to $Y^{\lambda\mu}_{(>)}$ at most proportional to $(n_o/\theta)^2$ as follows from the inequality (IV.58).
Then $Y^{\lambda\mu}_{(>)}(\vec{q},z)$ may be rewritten as

$$Y^{\lambda\mu}_{(>)}(\vec{q},z) = \frac{-\beta m}{8\pi^2 n_o} \frac{q^2}{(z+\nu_o q^2)^2} \int d\hat{k} \int_{N_o\theta}^{k_o} dk\, k\, \frac{S^{\lambda\mu}_{\eta}(\vec{k},-\vec{k})}{-z^{\lambda}_{k}-z^{\mu}_{l}} + O((n_o/\theta)^2) . \qquad \text{(IV.60)}$$

The term of order $(n_o/\theta)^2$ yields contributions to $C^{(e)}(z)$ at most proportional to $n_o \log(z_o/z)$, (compare (IV.53)).
In the cases where the labels λ , μ in (IV.60) are taken to be (++) , (−−) , (η+) , (η−) , (T+) , (T−) the inequality (IV.58) for the denominator in (IV.60) can be improved to

$$\cdot \quad | z_k^\lambda + z_l^\mu | > a\, c_o\, k \qquad (a>o) \qquad \text{(IV.61)}$$

valid for all values of k larger than $N_o\theta$. Here c_o is the adiabatic sound velocity. From this, the first term in (IV.60) can be estimated directly with the result

$$\cdot \quad \sum_\sigma Y_{(>)}^{\sigma T}(\vec{q},z) \sim \sum_\sigma Y_{(>)}^{\sigma\eta}(\vec{q},z) \sim \sum_\sigma Y_{(>)}^{\sigma\sigma}(\vec{q},z) \sim (n_o/\theta)^2 \,. \qquad \text{(IV.62)}$$

In summary we have from (IV.62), (IV.48b) and (IV.53)

$$\cdot \quad Y(\vec{q},z) = Y_{(>)}^{\eta\eta}(\vec{q},z) + Y_{(>)}^{+-}(\vec{q},z) + Y_{(>)}^{-+}(\vec{q},z) + O((n_o/\theta)^2) \,. \text{(IV.63)}$$

We still have to show that the dominant contributions to $Y(\vec{q},z)$ in (IV.42) arise from the shear-shear and the opposite sound modes.
We first calculate $Y_{(>)}^{\eta\eta}(\vec{q},z)$ from (IV.48a) and (IV.60), where

$$\cdot \quad S_\eta^{\eta\eta}(\vec{k},-\vec{k}) = 4(\beta m)^{-2}\, (\cos\varphi \sin\varphi)^2 \qquad \text{(IV.64)}$$

with $\cos\varphi = \hat{k}.\hat{q}$, and

$$\cdot \quad \frac{1}{-z_k^\eta - z_l^\eta} = \frac{1}{2\nu_o k^2} \{ 1 + O(q/k) \} \,. \qquad \text{(IV.65)}$$

The correction term of order q/k does not contribute to the leading singularity of $Y_{(>)}^{\eta\eta}$, similarly as we have seen in (IV.59).
Performing the integrations in (IV.60) and using (IV.20) yields the final result

$$\cdot \quad Y^{\eta\eta}_{(>)}(\vec{q},z) = \frac{d_o(D_o+\nu_o)}{2\nu_o} \frac{q^2}{(z+\nu_o q^2)^2} \log(\theta/k_o) + O((n_o/\theta)^2) \ . \qquad \text{(IV.66)}$$

Note that the first term is of order $(n_o/\theta)^2 \log\theta$.
The amplitudes in (IV.60) for the opposite sound modes are obtained from (IV.48c)

$$\cdot \quad S^{+-}_{\eta}(\vec{k},-\vec{k}) = S^{-+}_{\eta}(\vec{k},-\vec{k}) = (\beta m)^{-2} \, (\cos\varphi\sin\varphi)^2 \ , \qquad \text{(IV.67)}$$

where $\cos\varphi = \hat{k}.\hat{q}$. The frequency denominators in the integrand of (IV.60) are for these cases given by

$$\cdot \quad \frac{1}{-z^+_k - z^-_l} = \frac{1}{ic_o(k-l)+\frac{1}{2}\Gamma_{so}(k^2+l^2)}$$

$$\cdot \quad \frac{1}{-z^-_k - z^+_l} = \frac{1}{-ic_o(k-l)+\frac{1}{2}\Gamma_{so}(k^2+l^2)} \ .$$

The factors $k^2 + l^2$ are replaced by $2k^2$, so that

$$\cdot \quad \frac{1}{-z^+_k - z^-_l} = \frac{1}{ic_o(k-l)+\Gamma_{so}k^2} \{ \ 1 + O(q/k) \ \}$$

$$\cdot \quad \frac{1}{-z^-_k - z^+_l} = \frac{1}{-ic_o(k-l)+\Gamma_{so}k^2} \{ \ 1 + O(q/k) \ \} \ ,$$

where the correction terms of order q/k give contributions to $Y^{+-}_{(>)}$ and $Y^{-+}_{(>)}$ of order $(n_o/\theta)^2$.
For fixed values of q and large values of k , the factor $k - l$ may *not* be replaced by zero. For this quantity we use the relation $k - l = q \cos\varphi + q \, O(q/k)$. This yields

$$\cdot \quad \frac{1}{-z^+_k - z^-_l} = \frac{1}{ic_o q\cos\varphi+\Gamma_s k^2} \{ \ 1 + O(q/k) \ \} \qquad \text{(IV.68a)}$$

$$\frac{1}{-z_k^- - z_l^+} = \frac{1}{-ic_o q\cos\varphi + \Gamma_s k^2}\ \{\ 1 + O(q/k)\ \}\ . \tag{IV.68b}$$

Strictly speaking these relations are valid only for $\cos\varphi \neq o$. We omit the proof that they may be used for $\cos\varphi = o$ too.
Substitution of (IV.67,68) into (IV.60) yields the final result for the opposite sound modes

$$Y^{+-}_{(>)}(\vec{q},z) + Y^{-+}_{(>)}(\vec{q},z) = \frac{d_o(D_o+\nu_o)}{4\Gamma_{so}}\ \frac{q^2}{(z+\nu_o q^2)^2}\ \log a(q,z) + O((n_o/\theta)^2)\ , \tag{IV.69a}$$

where

$$a(q,z) = \begin{cases} z/z_o & \text{if } N_o^2 z > c_o q \\ q/k_o & \text{if } N_o^2 z < c_o q \end{cases}\ . \tag{IV.69b}$$

The leading non-analytic behaviour of $C^{(e)}(z)$ is obtained from (IV.41, 63,66,69) with the result

$$C^{(e)}(z) = -\tfrac{1}{2}\, d_o^2\ \{\ \frac{1}{4\nu_o} + \frac{1}{8\Gamma_{so}}\ \}\ \{\ (\log(z_o/z))^2 + O(\log z_o/z)\ \}\ . \tag{IV.70}$$

Its inverse Laplace transform is given by

$$\tilde{C}^{(e)}(t) = -\, d_o^2\ \{\ \frac{1}{4\nu_o} + \frac{1}{8\Gamma_{so}}\ \}\ \frac{1}{t}\ \{\ \log(t/t_o) + O(1)\ \}\ , \tag{IV.71}$$

which is our final result for this contribution to the velocity correlation function.

Next we consider the contribution $\tilde{C}^{(f)}(t)$ represented by diagram f in figure 11, and reading explicitly

$$\widetilde{C}^{(f)}(t) = n_o^{-1}\ (2\pi)^{-2} \sum_{\lambda} \int' d\vec{q}\ \exp(z_q^{\lambda} t)\ \widetilde{X}(\vec{q},t)$$

$$< v_{1x}\ (\Lambda^s)^{-1} < T_o(12)\ P_{-\vec{q}}^{\lambda}(2)\ P_{\vec{q}}^{s}(1)\ T_o(12) >_2\ (\Lambda^s)^{-1}\ v_{1x} >_1 , \tag{IV.72}$$

where λ runs over the hydrodynamic modes (T,σ,η) and the Laplace transform of $\widetilde{X}(\vec{q},t)$ reads according to figure 11f

$$X(\vec{q},z) = \sum_{\mu} X^{\mu}(\vec{q},z) \tag{IV.73}$$

$$X^{\mu}(\vec{q},z) = n_o\ (z+D_o q^2)^{-2}\ (2\pi)^{-2} \int' d\vec{k}\ (z-z_k^s-z_l^{\mu})^{-1}\ N^{\mu}(\vec{k},\vec{l}) \tag{IV.74}$$

$$N^{\mu}(\vec{k},\vec{l}) = < \widetilde{\varphi}_{\vec{q}}^{s}(\vec{v}_1)\ |\ < T_o(23)\ P_{\vec{k}}^{s}\ P_{\vec{l}}^{\mu}(3)\ T_o(23) >_3\ |\ \varphi_{\vec{q}}^{s}(\vec{v}_1) >_1 , \tag{IV.75}$$

where $\vec{l} = \vec{q}-\vec{k}$ and $\mu = (T,\sigma,\eta)$.
The quantity on the second line of (IV.72) is studied in (IV.36) and (IV.37). Due to the same arguments given there only the shear mode $(\lambda=\eta)$ contributes in (IV.72) to the dominant long time behaviour of $\widetilde{C}^{(f)}(t)$. Then it follows from (IV.16) that

$$\widetilde{C}^{(f)}(t) = (\beta m n_o)^{-1}\ (2\pi)^{-2} \int' d\vec{q}\ (1-\hat{q}_x^2)\ e^{-\nu_o q^2 t}\ \widetilde{X}(\vec{q},t) . \tag{IV.76}$$

Its Laplace transform is given by

$$C^{(f)}(z) = (\beta m n_o)^{-1}\ (2\pi)^{-2} \int' d\vec{q}\ (1-\hat{q}_x^2)\ X(\vec{q},z+\nu_o q^2) . \tag{IV.77}$$

The function $X(\vec{q},z)$ is studied in a similar way as was done for $Y(\vec{q},z)$, compare (IV.42,43,44) with (IV.73,74,75).
The self diffusion modes at the beginning and at the end of (IV.75) are needed explicitly in *first* order in q . The matrix elements $N^{\mu}(\vec{k},\vec{l})$ are at least proportional to (cfr. (IV.45))

$$\cdot \quad N^{\mu}(\vec{k},\vec{l}) \sim (q/n_o)^2 \ . \tag{IV.78}$$

By taking the modes contained in $P^{S}_{\vec{k}}$ and $P^{\mu}_{\vec{l}}$ to *zeroth* order in $\vec{k}$ and $\vec{l}$ we find

$$\cdot \quad N^{\eta}(\vec{k},\vec{l}) = -\frac{q^2}{\beta m n_o^2}(\hat{q}_{\perp}.l)^2 \tag{IV.79}$$

$$\cdot \quad N^{T}(\vec{k},\vec{l}) = o \ . \tag{IV.80}$$

The functions $X^{\mu}(\vec{q},z)$ can be calculated according to the method given above, with the result

$$\cdot \quad X^{+}(\vec{q},z) \sim X^{-}(\vec{q},z) \sim (n_o/\theta)^2 \ , \tag{IV.81}$$

where $\theta(q,z)$ is the maximum of q and $\sqrt{z/D_o+\nu_o}$ according to (IV.50). The shear mode in (IV.74) gives

$$\cdot \quad X^{\eta}(\vec{q},z) = 2d_o \frac{q^2}{(z+D_o q^2)^2}\log(\theta/k_o) + O((n_o/\theta)^2) \ . \tag{IV.82}$$

Using these results we obtain

$$\cdot \quad C^{(f)}(z) = -\frac{1}{2} d_o^2 \frac{1}{D_o+\nu_o} \{ (\log(z_o/z))^2 + O(\log(z_o/z) \} \ . \tag{IV.83}$$

Its inverse Laplace transform is given by

$$\cdot \quad \tilde{C}^{(f)}(t) = - d_o^2 \frac{1}{D_o+\nu_o}\frac{1}{t} \{ \log(t/t_o) + O(1) \} \ , \tag{IV.84}$$

which is our final result for the contribution of diagram 11f.

The diagrams g and h do not contribute to the leading long time behaviour of $\tilde{C}(t)$ in this order in the density (n_o^2). To prove this statement the estimating procedure discussed below (IV.49) is very helpful.

As an illustration we consider diagram 11g. Taking the slowly decaying part of all internal propagators one finds an expression for $C^{(g)}(z)$ of the structure

$$. \quad C^{(g)}(z) \sim n_o^{-2} \int' d\vec{q} \int' d\vec{k} \frac{q}{z+D'q^2} \frac{1}{z+D'k^2+D''q^2+D'''l^2} \frac{k}{z+D'k^2} , \tag{IV.85}$$

where $\vec{l} = \vec{q}-\vec{k}$ and D' , D'' and D''' are quantities of order ν_o , D_{To} or D_o , and where we consider only hydrodynamic modes of diffusive type (η, T) . The factor q in the numerator of (IV.85) arises from the matrix element

$$. \quad < < \varphi^{s}_{\vec{q}}(\vec{v}_1)\ T_o(13)\ \varphi^{s}_{\vec{k}}(\vec{v}_1)\ \varphi^{\lambda}_{\vec{l}}(\vec{v}_3) >_1 >_3 ,$$

where the self diffusion mode at the beginning has to be taken to *first* order in q (compare (IV.44)), yielding a factor q. The factor k in the numerator of (IV.85) comes from

$$. \quad < < \varphi^{\lambda}_{\vec{l}}(\vec{v}_3)\ \varphi^{\mu}_{-\vec{q}}(\vec{v}_2)\ T_o(23)\ (1+P_{23})\ \varphi^{\lambda'}_{-\vec{k}}(\vec{v}_2) >_2 >_3 ,$$

where the last mode has to be taken to first order in k .

The estimating procedure given above applied to the expression (IV.85) yields

$$. \quad C^{(g)}(z) \sim n_o^{-2} \int_o^{k_o} dq\ q \frac{q}{z+D'q^2} \int_{N_o\theta}^{k_o} dk\ k \frac{1}{D'^2k^3} ,$$

so that

$$. \quad C^{(g)}(z) \sim n_o \log(z_o/z) . \tag{IV.86}$$

Similarly we find for diagram 11h

$$\cdot \quad C^{(h)}(z) \sim n_o \log(z_o/z) \ . \tag{IV.87}$$

So far we have studied the contributions to $C(z)$ up to first order in the density. Summarizing we have found in (IV.9,28,33,70,83,86,87) that for $z \ll z_o$

$$\cdot \quad C(z) = D_o + d_o \log(z_o/z) + \frac{1}{2} d_1 \left[\ (\log(z_o/z))^2 + O(\log(z_o/z)) \ \right]$$

$$+ O(n_o^2) \left[\ (\log(z_o/z)^3 + O((\log(z_o/z)^2) \ \right] \ , \tag{IV.88}$$

where the coefficients D_o , d_o , d_1 are of succeeding higher order in the density. The coefficient d_1 can be obtained from the results (IV. 70,83)

$$\cdot \quad d_1 = - d_o^2 \left[\ \frac{1}{D_o+\nu_o} + \frac{1}{4\nu_o} + \frac{1}{8\Gamma_{so}} \ \right] \tag{IV.89}$$

and is of first order in the density.
The terms in (IV.88) of type $n_o^2 \ (\log(z_o/z))^3$ arise from diagrams in which e.g. the slow Boltzmann propagator of the tagged particle in diagram 11e is replaced by the ring propagator. This follows directly by applying the methods given above.

The inverse Laplace transform of (IV.88) gives our final result for the velocity correlation function for $t \gg t_o$

$$\cdot \quad \widetilde{C}(t) = D_o \, \delta(t) + d_o \frac{1}{t} + d_1 \frac{1}{t} \{ \ \log(t/t_o) + O(1) \ \}$$

$$+ O(n_o^3) \ \frac{t_o}{t} \{ \ (\log(t/t_o))^2 + O(\log(t/t_o)) \ \} \ . \tag{IV.90}$$

Before concluding this section we calculate the time dependent diffusion coefficient $D^{(o)}(t)$ from (I.45) and (IV.90) yielding for $t \gg t_o$

$$D^{(o)}(t) = D_o + d_o \{ \log(t/t_o) + O(1) \} +$$

$$+ \frac{1}{2} d_1 \{ (\log(t/t_o))^2 + O(\log(t/t_o)) \} +$$

$$+ O(n_o^2) (\log(t/t_o))^3 . \qquad \text{(IV.91)}$$

b. The time dependent super Burnett coefficient

In this section the time dependent super Burnett coefficient is calculated from kinetic theory for a two dimensional hard disk system.

We start from the relations (I.46-50)

$$D^{(2)}(t) = E(t) - E_1(t) - E_2(t) - E_3(t) \; . \tag{IV.92}$$

The function E(t) is calculated by means of the diagrammatic representation described in section *d* of chapter II.
The functions $E_i(t)$ (i=1,2,3) can be calculated from the relations (I.48-50) and the results for the velocity correlation function obtained in the previous section.

In principle we order the contributions to E(t) and $E_i(t)$ with respect to their long time behaviour. Then it will appear that there exists a series of contributions to these functions, which are increasingly more divergent in time with coefficients, which are of increasingly higher order in the density.
Therefore it is more convenient to order the contributions first with respect to their density dependence and to study then, within each order in the density, the terms, which are dominant in time.
In successive orders in the density the dominant long time behaviour turns out to be more divergent and therefore it is predicted correctly by the kinetic theory used here, according to the discussion in sections II*a* and III*c*.
This procedure is similar to the way the velocity correlation function was studied in section *a*.
First we apply this procedure to order the contributions of the subtracted terms $E_i(t)$ in (IV.92).

For both velocity correlation functions in the expression (I.50) for $E_3(t)$ the expansion (IV.1) for $\tilde{C}(t)$ is substituted yielding

$$\cdot \quad E_3(t) = \sum_{r,s} E_3^{(r,s)}(t) \tag{IV.93}$$

$$\cdot \quad E_3^{(r,s)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \, \tilde{C}^{(r)}(t_3) \, \tilde{C}^{(s)}(t_2-t_1) \; , \tag{IV.94}$$

where r and s label the diagrams occurring in figure 11 (r,s=B,R,c,d, e,f,...).

Each diagram of figure 11 or equivalently each term in the expansion (IV.1) has a well defined density dependence when time is measured in units t_o , which can be obtained from the relation (IV.3).

Consequently to lowest order in the density $E_3(t)$ is described by the term $E_3^{(B,B)}(t)$ in (IV.93). Its time dependence is obtained from the result (IV.9) for $\tilde{C}^{(B)}(t)$, hence

$$\cdot \quad E_3^{(B,B)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \, \tilde{C}^{(B)}(t_3) \, \tilde{C}^{(B)}(t_2-t_1)$$

$$\sim n_o^{-3} \, \mathcal{O}((t/t_o)^o) \; . \tag{IV.95}$$

To next order in the density we find two contributions to $E_3(t)$ namely $E_3^{(R,B)}(t)$ and $E_3^{(B,R)}(t)$. The time dependence can be obtained from the results (IV.9,27) for $\tilde{C}^{(B)}(t)$ and $\tilde{C}^{(R)}(t)$, hence

$$\cdot \quad E_3^{(R,B)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \, \tilde{C}^{(R)}(t_3) \, \tilde{C}^{(B)}(t_2-t_1)$$

$$\sim n_o^{-2} \, \mathcal{O}(t/t_o) \tag{IV.96}$$

and

$$. \quad E_3^{(B,R)}(t) \sim n_o^{-2}\, \mathcal{O}((t/t_o)^o) \; . \qquad \text{(IV.97)}$$

Note that $E_3^{(R,B)}(t)$ diverges as t tends to infinity and $E_3^{(B,R)}(t)$ stays finite.

Then we collect the terms in (IV.93), which are of order n_o^{-1} and we find

$$. \quad E_3^{(r,s)}(t) \sim n_o^{-1} \quad \text{if} \quad \begin{cases} r=B;\ s=c,d,\ldots,h \\ r=R;\ s=R \\ r=c,d,\ldots,h;\ s=B \end{cases} . \qquad \text{(IV.98)}$$

The time dependence of these expressions is obtained from the results of the previous section (IV.9,27,33,71,84,86,87) yielding

$$. \quad E_3^{(B,s)}(t) \sim n_o^{-1}\, \mathcal{O}((t/t_o)^o) \qquad \text{if } s=c,d,\ldots,h$$

$$. \quad E_3^{(R,R)}(t) \sim n_o^{-1}\, \mathcal{O}(t/t_o \log(t/t_o))$$

$$. \quad E_3^{(c,B)}(t) + E^{(d,B)}(t) \sim n_o^{-1}\, \mathcal{O}(t/t_o)$$

$$. \quad E_3^{(e,B)}(t) \sim n_o^{-1}\, \mathcal{O}(t/t_o \log(t/t_o))$$

$$. \quad E_3^{(f,B)}(t) \sim n_o^{-1}\, \mathcal{O}(t/t_o \log(t/t_o))$$

$$. \quad E_3^{(g,B)}(t) \sim E_3^{(h,B)}(t) \sim n_o^{-1}\, \mathcal{O}(t/t_o) \qquad \text{(IV.99)}$$

and we conclude that in this order in the density there are three contributions, which are dominant in time namely $E_3^{(R,R)}(t)$, $E_3^{(e,B)}(t)$ and $E_3^{(f,B)}(t)$.

In summary, $E_3(t)$ has the structure

$$. \quad E_3(t) = n_o^{-3}\, \mathcal{O}((t/t_o)^o) + n_o^{-2}\, \mathcal{O}(t/t_o) + n_o^{-1}\, \mathcal{O}(t/t_o \log(t/t_o)) + \ldots \; . \qquad \text{(IV.100)}$$

We will show in this section that the function $E(t)$ contains contributions, which cancel systematically the terms $E_3^{(R,B)}(t)$, $E_3^{(R,R)}(t)$, $E_3^{(e,B)}(t)$ and $E_3^{(f,B)}(t)$, when substituted in the relation (IV.92) for $D^{(2)}(t)$.

The contributions to the function $E_2(t)$ defined by (I.49) are given by a similar relation as (IV.93,94), namely

$$. \quad E_2(t) = \sum_{r,s} E_2^{(r,s)}(t)$$

$$. \quad E_2^{(r,s)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \, \tilde{C}^{(r)}(t_2) \, \tilde{C}^{(s)}(t_3-t_1) \; . \quad \text{(IV.101)}$$

From the results of the previous section one finds that $E_2(t)$ is of the form

$$. \quad E_2(t) = n_o^{-3} \, \mathcal{O}((t/t_o)^o) + n_o^{-2} \, \mathcal{O}((t/t_o)^o) + n_o^{-1} \, \mathcal{O}(t/t_o) + \ldots \; . \quad \text{(IV.102)}$$

Note that the more dominant terms of the form $n_o^{-2}\, \mathcal{O}(t/t_o)$ and n_o^{-1} $\mathcal{O}(t/t_o \log(t/t_o))$ are absent in $E_2(t)$, (compare (IV.100)).

The function $E_1(t)$ defined by (I.48) can be studied in a similar way. However we will show that $E_1(t)$, when substituted in the relation (IV.92) for $D^{(2)}(t)$, cancels completely a term contained in $E(t)$.

Explicitly we will find in this section that the super Burnett coefficient is of the form

$$. \quad D^{(2)}(t) = n_o^{-3} \, \mathcal{O}((t/t_o)^o) + n_o^{-2} \, \mathcal{O}(t/t_o) + n_o^{-1} \, \mathcal{O}(t/t_o \log(t/t_o)) + \ldots \; . \quad \text{(IV.103)}$$

Therefore in the course of the calculation we neglect consistently contributions to $D^{(2)}(t)$, i.e. to $E(t)$ and $E_i(t)$, which are, in any order in the density, smaller in time than the dominant ones indicated here.
Consequently the subtracted term $E_2(t)$ in (IV.92) may be neglected in order n_o^{-2} and n_o^{-1} , as follows from (IV.102).

Next we consider the density dependence of diagrams contribution to $E(t)$ by means of the relation (III.66). For d=2 this density dependence is given by

$$. \quad n_o^{-3}\, n_o^{N_1+N_2} \tag{IV.104}$$

valid when time is measured in units t_o and where N_1 and N_2 are the numbers of vertices of type 1 and 2 given in figure 2.

The diagrams contributing to $E(t)$ as defined in section *d* of chapter II are divided into five classes (I,...,V), drawn schematically in figure 5, so that

$$. \quad E(t) = E_{(I)}(t) + \ldots + E_{(V)}(t) \ . \tag{IV.105}$$

The double straight line in figure 5 represents the full propagator $\overline{\Gamma}_o^s(1,t)$ defined in (II.1), a cross represents the velocity of the tagged particle v_{1x} and the bubbles stand for the sum of all diagrams with one or two crosses in their interior and will be considered below.

Before starting the actual calculations we quote a useful estimate for the long time behaviour of the full propagator $\overline{\Gamma}_o^s(1,t)$.
This operator can be separated into a constant part and a remainder, referred to as the orthogonal part

$$\overline{\Gamma}_o^s(1,t) = P_o^s(1) + (1-P_o^s(1))\,\overline{\Gamma}_o^s(1,t) \,, \tag{IV.106}$$

where the projection operator $P_o^s(1)$ is defined by (II.51) and (II.37). We have used the fact that $P_o^s(1)$ projects on the unit function, which is an exact eigenfunction of $\overline{\Gamma}_o^s(1,t)$ with eigenvalue 1 .
An estimate for the orthogonal part of $\overline{\Gamma}_o^s(1,t)$ can be obtained from the considerations of the previous section. Especially from (IV.90) we find

$$\begin{aligned}(1-P_o^s(1))\,\overline{\Gamma}_o^s(1,t) &\sim n_o^o\,\delta(t/t_o)\,U_o(1) + \\ &+ n_o^1\,h_1(t/t_o)\,U_1(1) + n_o^2\,h_2(t/t_o)\,U_2(1) + \dots \,, \end{aligned}\tag{IV.107}$$

where $U_i(1)$ $(i=0,1,2,\dots)$ are regular time independent and density independent operators, acting on functions of $\vec{v}_1$, which are orthogonal to the unit function; $h_i(x)$ $(i=1,2\dots)$ are bounded functions of x , with an asymptotic behaviour for large x given by

$$h_i(x) \sim (\log x\,)^{i-1}/x \qquad (i=1,2,\dots)\,. \tag{IV.108}$$

We start the calculation of $E(t)$ with the term $E_{(V)}(t)$ in (IV.105). All diagrams of class V, in figure 5, together give a contribution

$$\begin{aligned}E_{(V)}(t) &= \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \\ &< v_{1x}\,\overline{\Gamma}_o^s(1,t_1)\,v_{1x}\,\overline{\Gamma}_o^s(1,t_2-t_1)\,v_{1x}\,\overline{\Gamma}_o^s(1,t_3-t_2)\,v_{1x} >_1 \,. \end{aligned}\tag{IV.109}$$

Due to the property (IV.2) the propagators $\overline{\Gamma}_o^s(1,t_1)$ and $\overline{\Gamma}_o^s(1,t_3-t_2)$ in this expression may be replaced by their orthogonal parts, as defined in (IV.106). We insert for $\overline{\Gamma}_o^s(1,t_2-t_1)$ in (IV.109) the decomposition (IV.106) so that

$$E_{(V)}(t) = E_{(V,A)}(t) + E_{(V,B)}(t) \ , \tag{IV.110}$$

where $E_{(V,A)}(t)$ arises from the constant part of $\overline{\Gamma}^s_o(1,t_2-t_1)$ and $E_{(V,B)}(t)$ from the orthogonal part.
From the relations (I.48), (II.6) and (IV.109) follows directly that

$$E_{(V,A)}(t) = E_1(t) \ , \tag{IV.111}$$

which is an exact relation valid for all times.
The function $E_{(V,A)}(t)$ is by itself the most important contribution to $E(t)$ for long times, but in the calculation of the time dependent super Burnett coefficient $D^{(2)}(t)$, it cancels the subtracted term $E_1(t)$, according to (IV.92).
An estimate for $E_{(V,B)}(t)$ can be obtained by using the relation (IV.107) for the orthogonal parts of all propagators in (IV.109), yielding for large times

$$E_{(V,B)}(t) \sim n_o^{-3}\, \mathcal{O}((t/t_o)^o) + $$

$$+ n_o^{-2}\, \mathcal{O}(\log(t/t_o)) + n_o^{-1}\, \mathcal{O}((\log(t/t_o))^2) + \ldots \ . \tag{IV.112}$$

We conclude therefore that the dominant long time contributions to $E_{(V)}(t)$ come from diagrams in subclass VA, which yield together a contribution $E_{(V,A)}(t)$ given by (IV.111).

The dominant *short* time behaviour of $E(t)$, for low densities, is obtained from diagram V (figure 5) if all full propagators $\overline{\Gamma}^s_o$ are replaced by Boltzmann propagators Γ^s_o, yielding for t on the order of t_o

$$E(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3$$

$$< v_{1x}\, \Gamma^s_o(1,t_1)\, v_{1x}\, \Gamma^s_o(1,t_2-t_1)\, v_{1x}\, \Gamma^s_o(1,t_3-t_2)\, v_{1x} >_1 \ . \tag{IV.113}$$

This expression can be calculated explicitly in successive Enskog approximations.
In first Enskog approximation the result for $D^{(2)}(t)$ is given by (III.37b), which is valid for any dimension. For d=2 the frequency λ_o is given by $\lambda_o = 1/t_o$ where t_o is given in (IV.4), so that for $t \sim t_o$

$$D^{(2)}(t) \simeq [D_o^{(2)}]_1 \{ 1 + \frac{3}{2} \exp(-t/t_o) - 4 \exp(-\frac{3}{2}t/t_o) + \frac{3}{2} \exp(-2t/t_o) - \frac{3}{2} (t/t_o) \exp(-t/t_o) - \frac{3}{4} (t/t_o)^2 \exp(-t/t_o) \} . \tag{IV.114}$$

Here $D_o^{(2)}$ is the Boltzmann value of the super Burnett coefficient, which in first Enskog approximation is given by

$$[D_o^{(2)}]_1 = \frac{2}{3} (\beta m)^{-2} t_o^3 . \tag{IV.115}$$

The expression (IV.114) illustrates qualitatively the short time behaviour of $D^{(2)}(t)$, which grows very slowly behaving initially as $\sim t^4$ and e.g. after $t = 4t_o$ it has reached only 70% of its asymptotic value.
Since the Enskog approximation scheme converges slowly for the super Burnett coefficient (Wood, private communication), the expression (IV.114) does not describe quantitatively the short time behaviour of $D^{(2)}(t)$.

Next we study the long time behaviour of diagrams occurring in class IV of figure 5.
The sum of all diagrams of class IV is equal to

$$E_{IV}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \int_{t_3}^t dt_4$$

$$< v_{1x}\, \overline{\Gamma}^{s}_{o}(t_1)\, v_{1x}\, \overline{\Gamma}^{s}_{o}(t_2-t_1)\, \overline{B}(t_3-t_2)\, \overline{\Gamma}^{s}_{o}(t_4-t_3)\, v_{1x} >_1 , \qquad (IV.116)$$

where the operator $\overline{B}(t_3-t_2)$ represents the bubble containing one cross in figure 5IV.
Following figure 6, the series expansion of $\overline{B}$

$$\overline{B}(t) = \overline{B}_{(A)}(t) + \overline{B}_{(B)}(t) + \ldots \qquad (IV.117)$$

gives a decomposition of class IV into subclasses IVA, IVB, ... According to section II*d* the diagrams in figure 6 can be constructed in an analogous way as those in figure 1.
Note that all operators in the expressions (IV.116,117) may be replaced by their orthogonal parts, as defined by (IV.106), because of the property (IV.2) and the fact that $\overline{B}$ always starts and ends with the operator $T_o(12)$.
The operator $\overline{B}_{(A)}(t)$ is explicitly given by

$$\overline{B}_{(A)}(t) = \int_o^t dt' \int d\vec{q}\, (2\pi)^{-2}\, n_o$$

$$< T_o(12)\, \overline{\Gamma}_{-\vec{q}}(2,t)\, \overline{\Gamma}^{s}_{\vec{q}}(1,t')\, v_{1x}\, \overline{\Gamma}^{s}_{\vec{q}}(1,t-t')\, T_o(12) >_2 . \qquad (IV.118)$$

First we study the operator $B_{(A)}(t)$, which is obtained from (IV.118) by replacing the full propagators by Boltzmann propagators such that

$$B_{(A)}(t) = \int_o^t dt' \int d\vec{q}\, (2\pi)^{-2}\, n_o$$

$$< T_o(12)\, \Gamma_{-\vec{q}}(2,t)\, \Gamma^{s}_{\vec{q}}(1,t')\, v_{1x}\, \Gamma^{s}_{\vec{q}}(1,t-t')\, T_o(12) >_2 . \qquad (IV.119)$$

This term is represented by the left hand side of the equation in figure 7.
The long time behaviour of $B_{(A)}(t)$ is obtained by replacing the fluid

propagator $\Gamma_{-\vec{q}}(2,t)$ in (IV.119) by its slowly decaying part $P_{-\vec{q}}(2)\ \Gamma_{-\vec{q}}(2,t)$, according to (II.54).
Following figure 7, the self propagators occurring in (IV.119) are decomposed into a slowly (s) and fastly (f) decaying part so that $B_{(A)}(t)$ falls apart into 4 terms

$$B_{(A)}(t) = B_{(A,ss)}(t) + B_{(A,fs)}(t) + B_{(A,sf)}(t) + B_{(A,ff)}(t)\ . \tag{IV.120}$$

The last operator of this set of four is a priori short ranged in time and will not be considered here. The operator $B_{(A,ss)}(t)$ (diagram ss in figure 7) is given by

$$\begin{aligned} B_{(A,ss)}(t) = n_o \int_o^t dt' \int' d\vec{q}\ (2\pi)^{-2} \sum_{j=1}^{4} \exp((z_q^j+z_q^s)t) \\ < T_o(12)\ \varphi^s_{\vec{q}}(\vec{v}_1)\,\varphi^j_{-\vec{q}}(\vec{v}_2) >_1\ >_2\ < \varphi^s_{\vec{q}}(\vec{v}_1)\ v_{1x}\ \varphi^s_{\vec{q}}(\vec{v}_1) >_1 \\ < < \varphi^s_{\vec{q}}(\vec{v}_1)\ \varphi^j_{-\vec{q}}(\vec{v}_2)\ T_o(12) >_2\ . \end{aligned} \tag{IV.121}$$

From (II.37), (II.39) and (IV.13) follows that

$$< \varphi^s_{\vec{q}}(\vec{v}_1)\ v_{1x}\ \varphi^s_{\vec{q}}(\vec{v}_1) >_1\ = -2iq_xD_o + O((q/n_o)^2)\ . \tag{IV.122}$$

To study the dominant long time behaviour of $B_{(A,ss)}(t)$ we insert the leading non-vanishing term in (IV.122) (i.e.$-2iq_xD_o$) into (IV.121), where the remaining hydrodynamic and self diffusion modes are taken in zeroth order in q , according to (II.37,40,43,46). Then the shear and heat mode give vanishing contributions in (IV.121) ($j=\eta,T$), due to the fact that the factor $2iq_xD_o$ is odd in q . The two sound modes together ($j=\sigma;\sigma=\pm 1$) give a contribution which can be estimated as

$$\cdot \quad B^{(+,-)}_{(A,ss)}(t) \sim n_o\, D_o\, t \int_0^{k_o} dq\, q^2 \sin(c_o qt)\, e^{-D'q^2t} \sim n_o^{\,2}(t_o/t)^2 \,, \tag{IV.123}$$

where D' stands for a typical diffusivity. This estimate is sufficient for our purpose.

For the shear and heat mode contributions we consider the second term in (IV.122) yielding

$$\cdot \quad B^{(\eta)}_{(A,ss)}(t) \sim B^{(T)}_{(A,ss)}(t) \sim n_o^{-1}\, t \int_0^{k_o} dq\, q^3\, e^{-D'q^2t} \sim n_o^2\, t_o/t \,. \tag{IV.124}$$

From this result and (IV.123) we find the estimate

$$\cdot \quad B_{(A,ss)}(t) \sim n_o^2\, t_o/t \,. \tag{IV.125}$$

Next we consider the long time behaviour of $B_{(A,fs)}(t)$ (figure 7) given by

$$\cdot \quad B_{(A,fs)}(t) = n_o \int_0^t dt'\ \delta(t') \int' d\vec{q}\ (2\pi)^{-2} \exp\{(z_q^j + z_q^s)t\}$$

$$< T_o(12)\ (1-P^s_{\vec{q}}(1))\ \{ i\vec{q}.\vec{v}_1 - n_o\Lambda^s\}^{-1}\ v_{1x}\ \varphi^s_{\vec{q}}(\vec{v}_1)\ \varphi^j_{-\vec{q}}(\vec{v}_2) >_1 >_2$$

$$< < \varphi^s_{\vec{q}}(\vec{v}_1)\ \varphi^j_{-\vec{q}}(\vec{v}_2)\ T_o(12) >_2 \,. \tag{IV.126}$$

After carrying out the time integration, one sees that $B_{(A,fs)}(t)$ has asymptotically the same time dependence as the ring contribution to the velocity correlation function but it is multiplied by an additional factor n_o ,

$$\cdot \quad B_{(A,fs)}(t) \sim n_o^2\, t_o/t \,. \tag{IV.127}$$

The same estimate holds for the operator $B_{(A.sf)}(t)$ occurring in figure 7, so that

$$\cdot \quad B_{(A.sf)}(t) \sim n_o^2\, t_o/t\ . \tag{IV.128}$$

Altogether we find for the operator $B_{(A)}(t)$

$$\cdot \quad B_{(A)}(t) \sim n_o^2\, t_o/t\ . \tag{IV.129}$$

One can dress the Boltzmann propagators in figure 7 with ring propagators, repeated ring propagators and so on, according to figure 1, to obtain an estimate for the full $\overline{B}_{(A)}$ operator, given by (IV.118). This procedure yields contributions to $\overline{B}_{(A)}(t)$, which are of higher order in the density but decaying more slowly in time, compared to (IV.129) and we find

$$\cdot \quad \overline{B}_{(A)}(t) \sim n_o^2\, t_o/t + n_o^3\, t_o/t\, \log(t/t_o) + \ldots\ . \tag{IV.130}$$

All this is very similar to the calculation of higher order contributions to the velocity correlation function, and the details are omitted here.
With the help of (IV.130) the contribution to E(t) of all diagrams of subclass IVA (figure 6) can be estimated, using (IV.116,117) and (IV.107,108),

$$\cdot \quad E_{(IV,A)}(t) \sim n_o^{-2}\, O(\log(t/t_o)) + n_o^{-1}\, O((\log(t/t_o))^2) + \ldots\ . \tag{IV.131}$$

The same procedure can be applied to the operators $\overline{B}_{(B)}(t)$, ... occurring in figure 6 and the expansion (IV.117). This will give no contributions to $E_{(IV)}(t)$, which exceed the estimate (IV.131). Therefore we have

$$\cdot \quad E_{(IV)}(t) \sim n_o^{-2}\, \mathcal{O}(\log(t/t_o)) + n_o^{-1}\, \mathcal{O}((\log(t/t_o))^2) + \ldots\ , \tag{IV.132}$$

which is our final result for class IV. Note that terms of order n_o^{-3} are absent, according to (IV.104), since at least one vertex of type 1 is present in class IV.

It is clear from figure 5 that the same estimate holds for the sum of all diagrams of class III for $t \gg t_o$

$$\cdot \quad E_{(III)}(t) \sim n_o^{-2}\, \mathcal{O}(\log(t/t_o)) + n_o^{-1}\, \mathcal{O}((\log(t/t_o))^2) + \ldots\ . \tag{IV.133}$$

The sum of all diagrams of class II gives a contribution to $E(t)$ equal to

$$\cdot \quad E_{(II)}(t) = \int_o^t dt_1 \ldots \int_{t_4}^t dt_5$$

$$< v_{1x}\, \overline{\Gamma}_o^s(t_1)\, \overline{B}(t_2-t_1)\, \overline{\Gamma}_o^s(t_3-t_2)\, \overline{B}(t_4-t_3)\, \overline{\Gamma}_o^s(t_5-t_4)\, v_{1x} >_1 \ . \tag{IV.134}$$

The estimates (IV.107) and (IV.130) for $\overline{\Gamma}_o^s$ and $\overline{B}$ are applied so that

$$\cdot \quad E_{(II)}(t) \sim n_o^{-1}\, \mathcal{O}((\log(t/t_o))^2) + \ldots\ . \tag{IV.135}$$

Here terms of order n_o^{-3} and n_o^{-2} are absent according to (IV.104).

Finally we consider the diagrams contributing to $E(t)$ and belonging to class I of figure 5.
According to figure 8, class I is decomposed into subclasses denoted by IA, IB, IC, ... Subclass IC can be obtained from IB by placing both crosses inside one bubble.
According to (IV.104) class I contains no diagrams proportional to

n_o^{-3} . There is one diagram of order n_o^{-2} , which is drawn on the left hand side of the equation in figure 9. It belongs to subclass IA and is denoted by IA.1.

The contribution $E_{(IA.1)}(t)$ reads explicitly, according to figure 9

$$\cdot \quad E_{(IA.1)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \; n_o^{-1} \; (2\pi)^{-2} \int d\vec{q}$$

$$< v_{1x} \; (\Lambda^s)^{-1} < T_o(12) \; \Gamma_{-\vec{q}}(2,t_3) \; \Gamma_{\vec{q}}^s(t_1) \; v_{1x}$$

$$\Gamma_{\vec{q}}^s(t_2-t_1) \; v_{1x} \; \Gamma_{\vec{q}}^s(t_3-t_2) \; T_o(12) >_2 (\Lambda^s)^{-1} \; v_{1x} >_1 , \qquad \text{(IV.136)}$$

where we have used already that only the fastly decaying parts of the initial and final Boltzmann self propagators in figure 9 contribute. The decomposition of the remaining three self propagators into a slowly (s) and fastly (f) decaying part yields 8 contributions to $E_{(IA.1)}(t)$, some of which are indicated on the right hand side of the equation in figure 9, so that

$$\cdot \quad E_{(IA.1)}(t) = E_{(IA.1sss)}(t) + E_{(IA.1sfs)}(t) + \ldots . \qquad \text{(IV.137)}$$

To obtain the long time behaviour of these functions it is sufficient to consider the slowly decaying part of the fluid propagator in (IV.136) only.
The first term in (IV.137) reads, according to figure 9

$$\cdot \quad E_{(IA.1sss)}(t) = \int_o^t dt_3 \int_o^{t_3} dt_2 \int_o^{t_2} dt_1 \; n_o^{-1} \; (2\pi)^{-2} \int' d\vec{q} \sum_{j=1}^{4}$$

$$\exp\{(z_q^j + z_q^s)t_3\} \; \{ < v_{1x} \; \varphi_{-\vec{q}}^j \; \varphi_{\vec{q}}^s >_1 \}^2 \; \{ < \varphi_{\vec{q}}^s \; v_{1x} \; \varphi_{\vec{q}}^s >_1 \}^2 , \qquad \text{(IV.138)}$$

where we have applied the property (II.57).
The leading long time behaviour arises from the shear mode contribution ($j=\eta$) . This is due to arguments discussed in (IV.15-27). From (IV.16) and (IV.122) one finds straightforwardly

$$\cdot \quad E_{(IA.1sss)}(t) = -\frac{1}{2}\, d_o\, t_o \frac{D_o^2}{D_o+\nu_o} [\ t/t_o + O((t/t_o)^o)\ ] \ , \qquad \text{(IV.139)}$$

where the quantity d_o is given by (IV.20). Next we consider the contribution (sfs) in figure 9.
In this case the intermediate Boltzmann self propagator in (IV.136) is fastly decaying. Then from (II.39) and (II.53) follows that

$$\cdot \quad P^s_{\vec{q}}\, v_{1x}\, (1-P^s_{\vec{q}})\, \Gamma^s_{\vec{q}}(t_2-t_1)\, v_{1x}\, P^s_{\vec{q}}$$

$$= P^s_{\vec{q}}\, \delta(t_2-t_1)\, D_o\ \{\ 1 + O(q/n_o)\ \} = P^s_{\vec{q}}\, \tilde{C}^{(B)}(t_2-t_1)\ \{\ 1 + O(q/n_o)\ \}\ , \qquad \text{(IV.140)}$$

where the last equality follows from (IV.9). Substitution of this result into (IV.136) yields

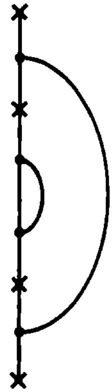
$$\cdot \quad E_{(IA.1sfs)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3\ \tilde{C}^{(B)}(t_2-t_1)\ n_o^{-1}\ (2\pi)^{-2}$$

$$\sum_{j=1}^{4} \int' d\vec{q}\ (1+O(q/n_o))\ \exp\{(z^j_q+z^s_q)t_3\}\ \{\ <\ v_{1x}\ \varphi^j_{-\vec{q}}\ \varphi^s_{\vec{q}}\ >_1\ \}^2\ . \qquad \text{(IV.141)}$$

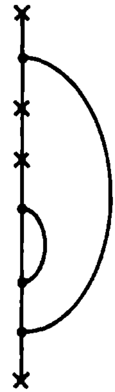
By comparing this relation with (IV.14) one sees that the dominant long time behaviour is described by

$$\cdot \quad E_{(IA.1sfs)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3\ C^{(R)}(t_3)\ C^{(B)}(t_2-t_1)$$

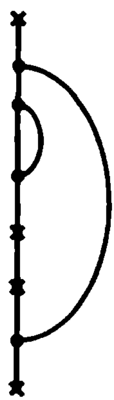
$$= E_3^{(R,B)}(t)\ , \qquad \text{(IV.142)}$$



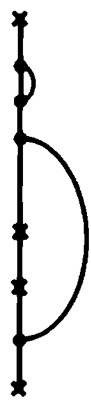
IA.3



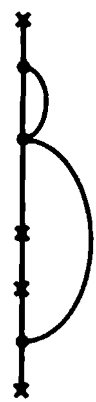
IA.4



IA.5



IA.6



IC.1

figure 12 : Diagrams contributing to the super Burnett coefficient to order n_o^{-1} for a two dimensional system.

where $E_3^{(R,B)}(t)$ is defined by (IV.94), and is of order $n_o^{-2}\ t/t_o$ (compare (IV.96)).

The contribution (fss) to $E_{(IA.1)}(t)$ (see figure 9) contains one factor $< \varphi^s_{\vec q}\ v_{1x}\ \varphi^s_{\vec q} >_1$ in the integrand of (IV.136). The leading non-vanishing term in this matrix element (i.e. $-2iq_x D_o$) is odd in q (compare the discussion below (IV.122)), and hence diagram (fss) is estimated as

$$\cdot \quad E_{(IA.1fss)}(t) \sim n_o^{-2}\ \mathcal{O}((t/t_o)^o)\ . \qquad \text{(IV.143)}$$

It is clear that the same estimate holds for $E_{(I.A.sff)}(t)$.

The remaining contributions (ffs) (fsf) (sff) and (fff) involve at least two δ functions of time in the threefold time integration given in (IV.136) and are hence estimated to be of order $(t/t_o)^o$ for large t .

So far we have studied the first diagram of class I and we found, to order n_o^{-2} in the density, two leading contributions to E(t) , which diverge proportional to t , so that

$$\cdot \quad E_{(IA.1)}(t) = E_3^{(R,B)}(t) - \frac{1}{2}\, d_o\, t_o\, \frac{D_o^2}{D_o+\nu_o} [\ t/t_o + \mathcal{O}((t/t_o)^o)\ ]\ , \qquad \text{(IV.144)}$$

which is our final result for diagram IA.1.

We finally consider in this section a set of diagrams belonging to class I, which contributes to the dominant long time behaviour of $D^{(2)}(t)$ in next order in the density (n_o^{-1}) . These are the diagrams IA.2, drawn in figure 10, IA.3-6 and IC.1 drawn in figure 12 and diagrams IA.7 and IC.2, which can be obtained by reading IA.6 and IC.1 from the bottom to the top. The diagrams IA.2-7 belong to subclass IA drawn in figure 8, IC.1 and IC.2 belong to subclass IC.

In fact *all* diagrams yielding contributions to E(t) of order n_o^{-1} can be obtained by attaching in any possible way two intermediate crosses to the diagrams c,d,e,f,g,h ... of figure 11, and by taking the slowly as well as the fastly decaying parts of the Boltzmann propagators involved. The resulting figures belong to one of the classes I-V drawn in figure 5. Those belonging to the classes I-IV were considered above. Some of the diagrams belonging to class I and which do not contribute to the leading long time behaviour of $D^{(2)}(t)$ are discussed below.

We start the calculation with $E_{(IA.2)}(t)$ represented by the left hand side of the equation in figure 10. By comparing the structure of diagram IA.2 with IA.1 (figure 9) it is clear that an analytic expression for $E_{(IA.2)}(t)$ can be obtained from the relation (IV.136) for $E_{(IA.1)}(t)$ by replacing the fluid propagator $\Gamma_{-\vec{q}}(2,t_3)$ in (IV.136) by the operator $\Upsilon_{-\vec{q}}(2,t_3)$ defined by (IV.35), so that

$$\cdot \quad E_{(IA.2)}(t) = \int_o^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \; n_o^{-1} \; (2\pi)^{-2} \int' d\vec{q}$$

$$< v_{1x} \; (\Lambda^s)^{-1} < \; T_o(12) \; \Upsilon_{-\vec{q}}(2,t_3) \; \Gamma^s_{\vec{q}}(t_1) \; v_{1x}$$

$$\Gamma^s_{\vec{q}}(t_2-t_1) \; v_{1x} \; \Gamma^s_{\vec{q}}(t_3-t_2) \; T_o(12) >_2 (\Lambda^s)^{-1} \; v_{1x} >_1 . \qquad \text{(IV.145)}$$

Then the arguments below (IV.35) can be applied to this case also and one finds that in order to obtain the dominant long time behaviour of $E_{(IA.2)}(t)$ the operator Υ may be replaced by its contribution (compare (IV.38))

$$\cdot \quad \Upsilon_{-\vec{q}}(2,t_3) = P^{\eta}_{-\vec{q}}(2) \; \tilde{Y}(-\vec{q},t_3) \; ,$$

where the function $\tilde{Y}(q,t)$ is defined by (IV.39). Its Laplace transform

is explicitly given by (IV.63,66,69).
Following figure 10 the intermediate three Boltzmann self propagators in (IV.145) are decomposed into a slowly and fastly decaying part, yielding

$$\cdot \quad E_{(IA.2)}(t) = E_{(IA.2sss)}(t) + E_{(IA.2sfs)}(t) + \dots \,. \qquad \text{(IV.146)}$$

According to the arguments above, an expression for $E_{(IA.2sss)}(t)$ can be obtained from the relation (IV.138) for $E_{(IA.1sss)}(t)$ by taking $j=\eta$ and replacing $\exp(z^{\eta}_{q} t)$ by $\widetilde{Y}(-\vec{q},t)$ with the result

$$\cdot \quad E_{(IA.2sss)}(t) = \int_{0}^{t} dt_3 \int_{0}^{t_3} dt_2 \int_{0}^{t_2} dt_1 \; n_0^{-1} \; (2\pi)^{-2} \int' d\vec{q}$$

$$\exp(z^{s}_{q} t_3) \; \widetilde{Y}(-\vec{q},t_3) \; \{ \, < v_{1x} \, \varphi^{\eta}_{-\vec{q}} \, \varphi^{s}_{\vec{q}} >_1 \, \}^2 \; \{ \, < \varphi^{s}_{\vec{q}} \, v_{1x} \, \varphi^{s}_{\vec{q}} >_1 \, \}^2 \, . \qquad \text{(IV.147)}$$

From the relations (IV.63,66,69) for the Laplace transform $\widetilde{Y}(-\vec{q},t)$ and (IV.16,122) for the matrix elements the q integral can be performed straightforwardly with the result

$$\cdot \quad E_{(IA.2sss)}(t) = d_0^2 \; t_0 \, \frac{D_0^2}{D_0+\nu_0} \left(\frac{1}{4\nu_0} + \frac{1}{8\Gamma_{so}} \right) [\; t/t_0 \log(t/t_0) + O(t/t_0) \;] \, . \qquad \text{(IV.148)}$$

To obtain an expression for $E_{(IA.2sfs)}(t)$ we note that in this case the integrand of (IV.145) contains a factor

$$\cdot \quad \Gamma^{s}_{\vec{q}}(t_1) \; P^{s}_{\vec{q}} \; v_{1x} \; (1-P^{s}_{\vec{q}}) \; \Gamma^{s}_{\vec{q}}(t_2-t_2) \; v_{1x} \; P^{s}_{\vec{q}} \; \Gamma^{s}_{\vec{q}}(t_3-t_2)$$

$$= P^{s}_{\vec{q}} \, \exp(z^{s}_{q} t_3) \; \widetilde{C}^{(B)}(t_2-t_1) \; [\; 1 + O(q/n_0) \;] \;\; ,$$

where the equality follows from (IV.140). By substituting this relation into (IV.145) and by comparing the resulting expression with

(IV.34) for $\tilde{C}^{(e)}(t)$ one finds immediately

$$\bullet \quad E_{(IA.2sfs)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3\ \tilde{C}^{(e)}(t_3)\ \tilde{C}^{(B)}(t_2-t_1)$$

$$= E_3^{(e,B)}(t) \ , \qquad\qquad (IV.149)$$

where $E_3^{(e,B)}(t)$ is defined by (IV.93,94) and is of order $n_o^{-1}\ t/t_o$ $\log(t/t_o)$ (compare (IV.99)).

The remaining contributions to $E_{(I.A2)}(t)$ in (IV.146) are at most proportional to $n_o^{-1}\ t/t_o$.

In summary we find for the contribution of diagram IA.2 to E(t)

$$\bullet \quad E_{(IA.2)}(t) = E_3^{(e,B)}(t) +$$

$$+ d_o^2\ t_o \frac{D_o^2}{D_o+\nu_o} \left(\frac{1}{4\nu_o} + \frac{1}{8\Gamma_{so}} \right) [t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)] \ . \qquad (IV.150)$$

In order to obtain the dominant long time behaviour of the diagrams IA.3-7, IC.1 and IC.2 we make the following remarks:

- Only the shear modes in both fluid propagators involved in these diagrams have to be considered.
- The actual calculations are most easily performed in Laplace language.
- These diagrams contain a twofold integration over wave numbers, which may be denoted by $\vec{q}$ and $\vec{k}$ in the order as they occur in the explicit analytic expressions,
- these analytic expressions are of a similar form as (IV.41-44) and the considerations made in section a (IV.41-71) can be applied to these cases, that it is to say
- the values of k in the k integral may be restricted to the interval $N_o\theta < k < k_o$
- then, in the integrand of the k integral the frequency z may be

omitted and the wave vector $\vec{l} = \vec{q}-\vec{k}$ may be replaced by $-\vec{k}$. This is due to the fact that the sound modes are absent (compare(IV.59), (IV.65) and (IV.68)).

With the help of this procedure the explicit calculations can be done straightforwardly. We will omit the details and quote the results only.

The intermediate five Boltzmann self propagators occurring in diagram IA.3 of figure 12 are decomposed into a slowly and fastly decaying part. If all propagators are taken to be slowly decaying one finds

$$\cdot \quad E_{(IA.3sssss)}(t) = \frac{1}{3} d_o^2 t_o \frac{D_o^2}{(D_o+\nu_o)^2} [t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)] \; . \tag{IV.151}$$

There are two contributions to the leading long time behaviour of $E_{(IA.3)}(t)$ involving one fastly decaying part, namely

$$\cdot \quad E_{(IA.3sfsss)}(t) = E_{(IA.3sssfs)}(t)$$

$$= - \frac{1}{4} d_o^2 t_o \frac{D_o}{D_o+\nu_o} [t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)] \; . \tag{IV.152}$$

The next contribution is

$$\cdot \quad E_{(IA.3sfsfs)}(t) = E_3^{(R,R)}(t) + n_o^{-1} \mathcal{O}(t/t_o) \; , \tag{IV.153}$$

where $E_3^{(R,R)}(t)$ is defined by (IV.94).
Further contributions to $E_{(IA.3)}(t)$ are at most proportional to n_o^{-1} $\mathcal{O}(t/t_o)$ so that

$$\cdot \quad E_{(IA.3)}(t) = d_o^2 t_o \{ \frac{1}{3} \frac{D_o^2}{(D_o+\nu_o)^2} - \frac{1}{2} \frac{D_o}{D_o+\nu_o} \}$$

$$[t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)] + E_3^{(R,R)}(t) \; . \tag{IV.154}$$

Diagram IA.4 yields a contribution to E(t) equal to

$$\cdot \quad E_{(IA.4)}(t) = d_o^2\, t_o \left\{ \frac{1}{3} \frac{D_o^2}{(D_o+\nu_o)^2} - \frac{1}{4} \frac{D_o}{D_o+\nu_o} \right\}$$

$$[\, t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)\,] + \frac{1}{2} E_3^{(B,f)}(t) \; . \qquad \text{(IV.155)}$$

This expression results from

$$\cdot \quad E_{(IA.4sssss)}(t) = E_{(IA.3sssss)}(t)$$

$$\cdot \quad E_{(IA.4sfsss)}(t) = \frac{1}{2} E_3^{(B,f)}(t)$$

$$\cdot \quad E_{(IA.4ssfss)}(t) = E_{(IA.3sfsss)}(t) \; . \qquad \text{(IV.156)}$$

The contribution of diagram IA.5 equals exactly IA.4 as can be seen from figure 12

$$\cdot \quad E_{(IA.5)}(t) = E_{(IA.4)}(t) \; . \qquad \text{(IV.157)}$$

The contributions of the diagrams IA.6 and IC.1 in figure 12 are proportional to

$$\cdot \quad E_{(IA.6)}(t) \sim n_o^{-1} [\, t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)\,] \qquad \text{(IV.158)}$$

$$\cdot \quad E_{(IC.1)}(t) \sim n_o^{-1} [\, t/t_o \log(t/t_o) + \mathcal{O}(t/t_o)\,] . \qquad \text{(IV.159)}$$

The explicit analytic expression for $E_{(IA.6)}(t)$ contains a factor of type (IV.32) and for $E_{(IC.1)}(t)$ it contains a factor (IV.31). This can be seen from the structure of the diagrams.
As we have discussed below (IV.32) both factors are each others opposite and therefore the leading long time behaviour in (IV.158) and

(IV.159) cancels

$$\cdot \quad E_{(IA.6)}(t) + E_{(IC.1)}(t) \sim n_o^{-1}\, O(t/t_o) \; . \tag{IV.160}$$

The same arguments apply to IA.7 and IC.2, which are obtained from IA.6 and IC.1 by interchanging the upper and lower ring

$$\cdot \quad E_{(IA.7)}(t) + E_{(IC.2)}(t) \sim n_o^{-1}\, O(t/t_o) \; . \tag{IV.161}$$

So far we have considered all diagrams contributing to the leading long time behaviour of E(t) in order n_o^{-1} in the density.

There are many other diagrams contributing to E(t) terms at most proportional to $n_o^{-1}\, O(t/t_o)$.
For example the simplest diagram of class IB in figure 8, IB.1 is proportional to

$$\cdot \quad E_{(IB.1)}(t) \sim n_o^{-1}\, O\left((\log(t/t_o))^2\right) \; . \tag{IV.162}$$

This can be seen from the estimate (IV.129) for $B_{(A)}(t)$ since $E_{(IB.1)}(t)$ contains this operator twice.
One can attach two crosses to the inner structure of diagram g or h in figure 11. The explicit analytic expressions can be studied in a similar way as was done in (IV.85,86) yielding that such contributions are at most proportional to $n_o^{-1}\, O(t/t_o)$.

In summary we find from the results in this section for E(T) and $E_i(t)$ and the relation (IV.92) that the time dependent super Burnett coefficient $D^{(2)}(t)$ for $t >> t_o$ is given by

$$\cdot \quad D^{(2)}(t) = D_o^{(2)} + e_1 t + e_2 t \;\{\, \log(t/t_o) + O(1) \,\} +$$

$$+ \mathcal{O}(n_o^o)\ t/t_o(\log(t/t_o))^2 \ . \tag{IV.163}$$

The term of type $n_o^o\ t/t_o(\log(t/t_o))^2$ arises from diagrams in which e.g. a fluid propagator in diagram IA.3 (figure 12) is replaced by a ring operator.

Here $D_o^{(2)}$ is the Lorentz-Boltzmann value of the super Burnett coefficient, which in first Enskog approximation is given by (IV.115), and is of order n_o^{-3} in the density.

The coefficient e_1 in (IV.163) can be obtained from the result (IV.96,97) for $E_3(t)$ and (IV.144) for $E(t)$, so that

$$\cdot \quad e_1 = -\frac{1}{2}\, d_o \frac{D_o^2}{D_o+\nu_o} \ , \tag{IV.164}$$

where the coefficient d_o is given by (IV.20).

The quantity $e_1 t_o$ is of order n_o^{-2} in the density.

The coefficient e_2 is obtained from the result (IV.99) for $E_3(t)$ and (IV.150,154,155,157) for $E(t)$

$$\cdot \quad e_2 = -\, d_o^2 \frac{D_o}{D_o+\nu_o} \left\{ \frac{\nu_o}{D_o+\nu_o} - \frac{D_o}{8\Gamma_{so}} - \frac{D_o}{4\nu_o} \right\} , \tag{IV.165}$$

where $e_2 t_o$ is of order n_o^{-1} .

c. Discussion

In this chapter we have found the following expressions for the long time behaviour of the velocity correlations function $\tilde{C}(t)$ and the time dependent super Burnett coefficient $D^{(2)}(t)$ for two dimensional hard sphere systems at low densities.

- $$\tilde{C}(t) \simeq d_o/t + d_1/t \log(t/t_o) + \dots \tag{IV.166}$$

- $$D^{(2)}(t) \simeq D_o^{(2)} + e_1 t + e_2 t \log(t/t_o) + \dots , \tag{IV.167}$$

where the coefficients d_o , d_1 , e_1 and e_2 are given by (IV.20,89,164, 165) and $D_o^{(2)}$ is the Boltzmann value of the super Burnett coefficient. The quantities d_o , d_1 , ... and e_1 , e_2 , ... are of increasing order in the density. Each term represents to that order in the density the most dominant time behaviour.
For a given (sufficiently small) density the series are expected to be only meaningful in a limited range of times (if one exists), such that successive terms are of decreasing order in magnitude.
The restrictions on the results (IV.166) and (IV.167) are discussed now.

First it is of interest to have an estimate of the time, from where on the results (IV.166,167) are a meaningful representation of the time dependence of $\tilde{C}(t)$ and $D^{(2)}(t)$.
We consider therefore the term d_o/t in (IV.166), which originates from the ring contribution $\tilde{C}^{(R)}(t)$ to $\tilde{C}(t)$. To derive the result (IV.27) for $\tilde{C}^{(R)}(t)$ from the exact relation (IV.11), we have made the following approximations.
The Boltzmann propagator $\Gamma_o^s(t_1)$, which occurs under the time integral over t_1 in (IV.11), has been replaced by the approximate expression

$(1-P_o^s)\ (-n_o\Lambda^s)^{-1}\ \delta(t_1)$, following (II.53). In fact the operator $(1-P_o^s)\ \Gamma_o^s(t_1)$ is proportional to $\exp(-t_1/t_o)$ as was discussed in chapter II. Since a time integral over this operator behaves as $\{1-\exp(-t/t_o)\}$ one has to wait, e.g. for three mean free times before the exponential has reached 5% of its initial value. From now on we consider $3t_o$ as a typical time needed to justify the approximate relation (II.53) for $\Gamma_o^s(t_1)$, so that $t_1 > 3t_o$.
Similarly the substitution of $(1-P_o^s)\ (-n_o\Lambda^s)^{-1}\ \delta(t-t_2)$ for $\Gamma_o^s(t-t_2)$ in (IV.11) is allowed if $t-t_2 > 3t_o$.
As a next approximation we have restricted the values of q in the q integral of (IV.11) to the interval $o \leqslant q \leqslant k_o$. In section IIIc the remaining q integrals with $k_o \leqslant q \leqslant \sigma^{-1}$ are estimated to be proportional to $\exp\{-(t_2-t_1)/t_o\}$. Therefore t_2-t_1 has to be larger than $3t_o$ before those contributions may be neglected.
For q values in the interval $o \leqslant q \leqslant k_o$ only the slowly decaying parts of the intermediate self propagator $\Gamma^s_{-\vec{q}}(t_2-t_1)$ and the fluid propagator $\Gamma_{\vec{q}}(2,t_2-t_1)$ in (IV.12) were considered. For times $t_2-t_1 > 3t_o$ the fastly decaying parts may be neglected since they also decay proportional to $\exp\{-(t_2-t_1)/t_o\}$.
We conclude that the expression (IV.12) is a good approximation to (IV.11) for times $t > 9t_o$.
The arguments presented so far are valid for d=2 and d=3 .
Of all terms present in (IV.12) we have only calculated the dominant term (i.e. d_o/t) and omitted many other contributions (e.g. (IV.23) and (IV.26)). Those contributions may still be important for intermediate times ($t \sim 9t_o$) , but they decay more rapidly, at least with an extra factor t_o/t compared to the leading term d_o/t .

Next we consider the term $d_1/t\ \log(t/t_o)$ in (IV.166). This term arises from the diagrams e and f in figure 11.
Both Boltmann propagators involved at the beginning and at the end of

these diagrams may be replaced by the approximate expression (II.53) for times $t > 6t_o$. The resulting expressions for $\tilde{C}^{(e)}(t)$ and $\tilde{C}^{(f)}(t)$ given in (IV.34) and (IV.72) originate from diagrams with three internal self propagators and a twofold integration over wave numbers. We have first restricted the wave numbers to be smaller than k_o, and next separated the three internal self propagators into their slowly and fastly decaying parts. For the expressions (IV.34) and (IV.72) with three slow internal propagators to become dominant, a time of at least $9t_o$ is required. The errors made in restricting the integrations over wave numbers have also become insignificant in this time, according to the arguments given above. Therefore the result $d_1/t \log(t/t_o)$ gives the leading time dependence for times larger than $15t_o$.

In general one sees from these arguments that the higher order terms require in general a longer time to grow to their full asymptotic strength, as given by (IV.166), since they arise from more complicated dynamical events.

Similarly the term $e_1 t$ in the expansion (IV.167) is a meaningful representation of $D^{(2)}(t)$ for times $t > 15t_o$ and the term $e_2 t \log(t/t_o)$ for times $t > 21t_o$. This can be seen by comparing the structure of diagram IA.1 (figure 9) and diagrams IA.3-5 (figure 12) with the diagrams 11b and 11f respectively.

Secondly we mention that the results (IV.166) and (IV.167) for two dimensional systems are for a given (small) density restricted to times smaller than some upperbound such that the second term in (IV.166) is small compared to the first one, and the third term in (IV.167) is small compared to the second one and so on, so that

$$. \quad | \, d_1/d_o \log(t/t_o) \, | \ll 1 \qquad \text{(IV.168)}$$

$$\cdot \quad | \, e_2/e_1 \, \log(t/t_o) \, | \ll 1 \,. \tag{IV.169}$$

To obtain a numerical estimate we replace the Boltzmann values of the transport coefficients occurring in the expressions (IV.20,89, 164,165) for d_o , d_1 , e_1 and e_2 by their first Enskog approximations

$$\cdot \quad [D_o]_1 = [\nu_o]_1 = \frac{1}{3}[\Gamma_{so}]_1 = \frac{1}{2n_o\sigma\sqrt{\pi\beta m}} \tag{IV.170}$$

and we introduce the reduced density n^{*} as

$$\cdot \quad n^{*} \equiv \frac{V_o}{V} = \frac{1}{2}\sqrt{3}\, n_o\sigma^2 \,, \tag{IV.171}$$

where V_o is the close packed volume, and n^{*} is a real number between zero and one.
Then one finds

$$\cdot \quad d_1/d_o = -\frac{19}{192}\sqrt{3}\, n^{*} \tag{IV.172}$$

$$\cdot \quad e_2/e_1 = \frac{5}{96}\sqrt{3}\, n^{*} \,. \tag{IV.173}$$

Here the densities n^{*} are restricted to at least $n^{*} < 0.1$, as will be discussed below.
For densities $n^{*} \approx 0.1$ the result (IV.166) for $\tilde{C}(t)$ is restricted to times t for which $| \frac{19}{192}\sqrt{3}\, 0.1 \log(t/t_o) | < 0.1$ or $t < 1000t_o$.
This estimate also applies to the expansion for $D^{(2)}(t)$, since $D^{(2)}(t)$ itself also involves $\tilde{C}(t)$ and since (IV.169) gives a larger value for this upperbound.

Finally we consider the restriction on our results to low densities. As discussed already in chapter II and section IIIc the statistical correlations, which we have omitted in our low density kinetic theory, give corrections to our results, which are essentially on the order of σ/l_o, where σ represents the diameter of a hard disk and l_o the mean free path. Numerical values for σ/l_o as function of the reduced density are given in reference (Wood, 1974) for hard sphere systems and are quoted in table I.

d=2

$n^☆$	σ/l_o
1/2	4.36
1/3	1.94
1/5	0.90
1/10	0.38
1/18	0.20

d=3

$n^☆$	σ/l_o
1/2	10.02
1/3	4.30
1/5	1.88
1/10	0.76
1/18	0.39

table I : Ratio of hard core diameter σ to the mean free path l_o .

The results for d=3 are given for comparison. We note that for d=3 the reduced density is given by

$$n^☆ = \frac{V_o}{V} = \frac{1}{2}\sqrt{2}\, n_o \sigma^3 , \qquad \text{(IV.174)}$$

where V_o is the close packed volume.
As follows from table I the quantity σ/l_o is only small (<0.4) for densities $n^☆ < 0.1$ (d=2) or $n^☆ < 0.05$ (d=3). Therefore the results obtained in this and the previous chapter are restricted to densities, which are smaller than the numbers given above.

CHAPTER V

Mode coupling theory in three dimensions

a. Formulation of the theory

In this chapter we describe the phenomenological mode coupling theory (Kawasaki 1966; Kadanoff 1968; Ernst 1970; Pomeau 1973) as far as it is needed for the self diffusion process in three dimensions. This theory yields a set of coupled integral equations for the correlation function $\tilde{U}(k,t)$, defined in (I.59), which is known as the mode coupling formula.
The derivation of the mode coupling formula is based on phenomenological arguments, which apply independently of the specific form of the intermolecular forces or the density of the system considered.
We develop a perturbative scheme to solve the coupled set of integral equations, starting from the assumption that the Navier Stokes self diffusion coefficient exists (see (I.69a)).
The solutions obtained in this way are consistent with the formulation of Fick's law expressed in the relations (I.33,34,35), and contain apart from the results of Fick's law higher order corrections to the functions of interest in the self diffusion problem.
These corrections are finally compared with the results, obtained from kinetic theory in chapter III for a three dimensional hard sphere system at low densities.

Let us now describe the phenomenological mode coupling theory in more detail. The basic idea of this theory is that the time decay of the projected current correlation function $\tilde{U}(k,t)$ for values of k small compared to k_o , where k_o is an inverse microscopic correlation length, proceeds in two stages (Ernst 1970):

- *A fast kinetic process* towards a state close to local equilibrium determines the behaviour of $\tilde{U}(k,t)$ for times of the order of a microscopic correlation time t_o . In a dilute gas k_o^{-1} is on the order of the mean free path l_o and t_o is on the order of the mean free time between collisions; in a liquid k_o^{-1} is on the order of the range of the intermolecular forces, and t_o is the time a particle needs to traverse this distance.

- *A slow hydrodynamic process*, in which the state close to local equilibrium decays to over all equilibrium, determines the dominant behaviour of $\tilde{U}(k,t)$ for times larger than t_o . The time evolution of this state close to local equilibrium is determined by the time evolution of the five hydrodynamic modes of the fluid and the diffusive mode of the tagged particle.

From these assumptions one arrives at the following explicit formula for $\tilde{U}(k,t)$ (Kadanoff 1968; Kawasaki 1970b) for times $t \gg t_o$ and wave numbers $k \ll k_o$

$$\tilde{U}(\vec{k},t) \simeq V^{-1} \sum_{\vec{q}}{}' \sum_{\lambda} S^{\lambda d}(\hat{q},\vec{l}) \, \tilde{G}_{\lambda}(\vec{q},t) \, \tilde{G}(\vec{l},t) \, . \qquad (V.1)$$

The summation $\Sigma'_{\vec{q}}$ extends over all wave numbers $\vec{q}$ in the reciprocal lattice of the (finite) volume V , and $\vec{l} = \vec{k}-\vec{q}$. The prime on the summation sign indicates that $|\vec{q}| < k_o$. In an infinite system (which will be considered from now on) the summation $V^{-1} \Sigma'_{\vec{q}}$ may be replaced by $(2\pi)^{-3} \int' d\vec{q}$.

The parameter λ in (V.1) runs over all hydrodynamic modes of the fluid: the heat mode (T) , two opposite sound modes ($\sigma = \pm$) and two shear modes (η_1 and η_2) , and over the diffusive mode of the tagged particle (d) . These functions depend on the phases of all N particles.
To lowest order in k they are, in conventional notation, given by

(Kadanoff 1968; Ernst 1974)

- $a^{T}_{\vec{k}} = (n/(k_B c_p))^{\frac{1}{2}}\ s_{\vec{k}}$

- $a^{\sigma}_{\vec{k}} = (\beta/(2mn))^{\frac{1}{2}}\ \{\ c^{-1}\ p_{\vec{k}} + \sigma\ \hat{k}.\vec{g}_{\vec{k}}\ \}$ $\qquad (\sigma = \pm)$

- $a^{\eta_i}_{\vec{k}} = (\beta/(mn))^{\frac{1}{2}}\ \hat{k}^{(i)}_{\perp}.\vec{g}_{\vec{k}}$ $\qquad (i=1,2)$

- $a^{d}_{\vec{k}} = c_{\vec{k}}\ .$ $\qquad$ (V.2)

The set of unit vectors $\hat{k}$, $\hat{k}^{(1)}_{\perp}$ and $\hat{k}^{(2)}_{\perp}$ are mutually orthogonal; $c_{\vec{k}} = \exp(-i\vec{k}.\vec{r}_1)$ is the density of the tagged particle*) and $\vec{g}_{\vec{k}}$ is the microscopic momentum density; $s_{\vec{k}}$ is the microscopic entropy per particle, $p_{\vec{k}}$ the microscopic local pressure; the latter two are given as linear combinations of the microscopic energy density $e_{\vec{k}}$ and the microscopic number density of the *fluid* $n_{\vec{k}}$, i.e.

- $p_{\vec{k}} = (\partial p/\partial e)_n\ e_{\vec{k}} + (\partial p/\partial n)_e\ n_{\vec{k}}$

- $s_{\vec{k}} = (nT)^{-1}\ \{\ e_{\vec{k}} - h\ n_{\vec{k}}\ \}\ .$ $\qquad$ (V.3)

In the previous equations we have introduced the following equilibrium quantities:
the number density of the fluid n*), the pressure p , the energy density e , entropy per particle s , temperature T , $\beta = (k_B T)^{-1}$, the enthalpy per particle $h = (e+p)/n$ and the zero frequency adiabatic sound velocity c defined by $mc^2 = (\partial p/\partial n)_s$.

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*) In chapter I the density of the tagged particle was denoted by $n(\vec{k})$ and the equilibrium density of the fluid by n_o . Here we use the symbols $c_{\vec{k}}$ and n respectively.

The hydrodynamic modes $a^{\lambda}_{\vec{k}}$ in (V.2) reduce to the hydrodynamic modes of the Boltzmann equation (II.40,43,46) when all equilibrium quantities are replaced by their ideal gas values and the microscopic densities $e_{\vec{k}}$, $\vec{g}_{\vec{k}}$, $n_{\vec{k}}$, and $c_{\vec{k}}$ by respectively $\sqrt{n}\,\frac{1}{2}\,mv^2$, $\sqrt{n}\,m\vec{v}$, $\sqrt{n}$ and 1.

The quantities $S^{\lambda d}(\hat{q},\vec{l})$ in (V.1) are given in terms of the two mode amplitude $A^{\lambda d}(\hat{q},\vec{l})$ as

$$S^{\lambda d}(\hat{q},\vec{l}) = |\ A^{\lambda d}(\hat{q},\vec{l})\ |^2 \qquad \text{(V.4)}$$

with

$$A^{\lambda d}(\hat{q},\vec{l}) = \langle\ j^{*}_{\vec{k}}\ a^{\lambda}_{\vec{q}}\ a^{d}_{\vec{l}}\ \rangle\ , \qquad \text{(V.5)}$$

where $j_{\vec{k}} = \hat{k}.\vec{v}_1\ \exp(-i\vec{k}.\vec{r}_1)$ according to (I.56).
The S functions can be calculated directly from the relations (V.2).
The result to lowest order in the wave numbers $\vec{k}$, $\vec{q}$ and $\vec{l}$ reads

$$S^{\eta d}(\hat{q},\vec{l}) = \sum_i S^{\eta_i d}(\hat{q},\vec{l}) = (\beta mn)^{-1}\ (1-\hat{k}.\hat{q})^2$$

$$S^{\sigma d}(\hat{q},\vec{l}) = (2\beta mn)^{-1}\ (\hat{k}.\hat{q})^2\ . \qquad \text{(V.6)}$$

The remaining S functions are vanishing to lowest order in the wave numbers.

Finally the mode coupling equations contain the propagators $\widetilde{G}_{\lambda}(k,t)$ for the hydrodynamic modes of the fluid, which will be given later on, and the propagator $\widetilde{G}(k,t)$ for the diffusive mode of the tagged particle, which is itself defined in terms of the Laplace transform of $\widetilde{U}(k,t)$ as (I.57)

$$G(k,z) = \frac{1}{z+k^2\ U(k,z)} \quad . \tag{V.7}$$

Even if the $\tilde{G}_\lambda(k,t)$ are given, the set of equations (V.1) and (V.7) is not a closed set for $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$, since the Laplace transform $U(k,z)$ involves also the short time behaviour of $\tilde{U}(k,t)$.
The mode coupling theory assumes that this short time behaviour is given by a bare correlation function, which decays fast for all values of k . For the long times of interest ($t \gg t_o$) it can essentially be described as a delta function in time $\delta(t)$ with a coefficient D^* independent of k . We therefore have for the Laplace transform of $\tilde{U}(k,t)$

$$U(\vec{k},z) \approx D^* + \int_{t_o}^{\infty} dt\ e^{-zt}\ (2\pi)^{-3} \int' d\vec{q}\ \sum_\lambda$$

$$S^{\lambda d}(\hat{q},\hat{l})\ \tilde{G}_\lambda(\vec{q},t)\ \tilde{G}(\vec{l},t)\ , \tag{V.8}$$

which is only meaningful for values of z with $|z| \ll z_o = t_o^{-1}$, and $k \ll k_o$.
The constant D^* is determined by the requirement $U(o,o) = D$, the Fick's law diffusion constant. As already explained in chapter I, we are only interested in the solutions of the mode coupling equations in the region, where k approaches zero and t approaches infinity, such that k^2t remain finite; or equivalently in Laplace language in the region, where z and k approach zero such that z/k^2 is finite.

Our basic assumption is that the mode coupling equations describe the dominant singularities in the correlation functions $U(k,z)$, $\tilde{U}(k,t)$ and the hydrodynamic propagators $G(k,z)$, $\tilde{G}(k,t)$ for $k\to o$ and $z\to o$ with $z/(Dk^2) = \zeta$ is finite, or $k\to o$ and $t\to\infty$ with $Dk^2t = \tau$ is finite.

Before developing a systematic solution of these equations we make a preliminary investigation.
When k approaches zero, $U(k,\zeta k^2)$ approaches $U(o,o) = D$ and $\tilde{G}(k,t) =$

$\exp(-Dk^2t)$. The hydrodynamic propagators of the fluid are in the same approximation given by $\tilde{G}_\eta(k,t) \simeq \exp(-\nu k^2 t)$ and $\tilde{G}_\sigma(k,t) \simeq \exp(-i\sigma ckt - \frac{1}{2}\Gamma_s k^2 t)$, where Γ_s is the sound damping constant and ν the kinematic viscosity.

Using these propagators in (V.8) one finds the contribution of the (ηd) modes to $\Delta U(k,z) = U(k,z) - U(o,o)$ to be of the form $k\, h_1(\zeta)$ and the contribution of the(σd)modes of the form $k^2\, h_2(\zeta)$, where $h_1(\zeta)$ and $h_2(\zeta)$ here and in the sequel are finite functions of $\zeta = z/Dk^2$.

In the following we will systematically neglect terms of $O(k^2)$ in $U(k,z)$, so that in (V.8) only contributions from the (ηd) modes have to be considered, yielding for $k \ll k_o$ and $z \ll z_o$

$$U(\vec{k},z) = D^{☆☆} + \frac{1}{\beta mn(2\pi)^3} \int_{t_o}^{\infty} dt\; e^{-zt} \int' d\vec{q}\; \{ 1 - (\hat{k}.\hat{q})^2 \}$$

$$\tilde{G}_\eta(\vec{q},t)\; \tilde{G}(\vec{l},t) + O(k^2 h(\zeta)) \; . \qquad \text{(V.9)}$$

Here $D^{☆☆}$ includes the contributions for k=z=o from the(σd)modes.

Now we describe the systematic expansion method to solve the equations (V.7) and (V.9).

We define

$$\Delta U(k,z) \equiv U(k,z) - D \qquad \text{(V.10)}$$

and we have seen from our preliminary calculations that $\Delta U(k,\zeta Dk^2)$ is a small quantity (of order $k\, h(\zeta)$), which can be used in a perturbation expansion. In zeroth approximation

$$U^{(o)}(k,z) = U(o,o) = D$$

$$\Delta U^{(o)}(k,z) = o \; . \qquad \text{(V.11)}$$

By means of (V.7) we expand $G(k,z)$ in powers of the small quantity $\Delta U(k,\zeta Dk^2)$, yielding for finite $\zeta = z/(Dk^2)$

$$\cdot \quad Dk^2\, G(k,\zeta Dk^2) = (\zeta+1)^{-1} - D^{-1}\, \Delta U(k,\zeta Dk^2)\; (\zeta+1)^{-2} + O(k^2 h(\zeta))\ . \tag{V.12}$$

The zeroth approximation to the propagators $\tilde{G}(k,t)$ and $G(k,z)$ follows from (V.11)

$$\cdot \quad G^{(o)}(k,z) = 1/(z+Dk^2)$$

$$\cdot \quad \tilde{G}^{(o)}(k,t) = \exp(-Dk^2 t)\ . \tag{V.13}$$

The *first* order approximation to the functions $\Delta U(k,z)$, $U(k,z)$ and $G(k,z)$ is obtained by inserting the *zeroth* order propagator $\tilde{G}^{(o)}(k,t)$ into (V.9), yielding at fixed values of ζ

$$\cdot \quad \Delta U^{(1)}(k,z) = \frac{1}{\beta mn(2\pi)^3} \int_{t_o}^{\infty} dt\ e^{-zt} \int' d\vec{q}\ \{1-(\hat{k}.\hat{q})^2\}\ e^{-Dl^2 t}\ \tilde{G}_{\eta}(q,t)$$

$$- \operatorname{Lim}_o(\text{first term}) + O(k^2 h(\zeta)) \tag{V.14}$$

$$\cdot \quad U^{(1)}(k,\zeta Dk^2) = D + \Delta U^{(1)}(k,\zeta Dk^2) \tag{V.15}$$

$$\cdot \quad Dk^2 G^{(1)}(k,\zeta Dk^2) = (\zeta+1)^{-1} - D^{-1}\, \Delta U^{(1)}(k,\zeta Dk^2)\; (\zeta+1)^{-2} + O(k^2 h(\zeta))\ , \tag{V.16}$$

where $\operatorname{Lim}_o(\ldots)$ represents at fixed ζ the k=o limit of the first term on the right hand side of (V.14). In principle one can go on in this way, but we restrict ourselves to the first approximation. It will be verified below that this approximation is sufficient to obtain the behaviour of $U(k,\zeta Dk^2)$ and $Dk^2 G(k,\zeta Dk^2)$ up to order $k^2\, h(\zeta)$.

In order to evaluate (V.14) we use a result for $G_\eta(k,z)$, obtained by Ernst and Dorfman (Ernst 1974) from the mode coupling theory applied to the case of the general fluid, valid for small k and $z/k^2 = \zeta$ finite

$$G_\eta(k,z) = (z+\nu k^2)^{-1} + \sum_{n=1}^{\infty} \Delta_\eta(n)\, k^{2+p_n}\, (z+\nu k^2)^{-2} + O(k^{-1}h(\zeta)) \,. \tag{V.17}$$

Here ν is the kinematic viscosity given by $\nu = \eta/(mn)$, where η is the shear viscosity, and

$$p_n = 1 - 2^{-n} \,. \qquad (n=1,2,\ldots) \tag{V.18}$$

Expressions for the coefficients $\Delta_\eta(n)$ are given in reference (Ernst 1972b, 1974) and we quote only the formula for n=1

$$\Delta_\eta(1) = \frac{c^{1/2}}{77\,\pi\, 2^{1/2}\, \beta mn\, \Gamma_s^{3/2}} \,. \tag{V.19}$$

Here Γ_s is the sound damping constant given by

$$\Gamma_s = (\gamma-1)\,\lambda\,/\,(nc_p) + (\tfrac{4}{3}\eta+\zeta)\,/\,(mn) \,, \tag{V.20}$$

where $\gamma = c_p/c_V$, λ is the heat conductivity, and ζ is the bulk viscosity; ζ vanishes at low densities (compare (II.45)).

Before starting the actual calculations we want to check the consistency of our approximation scheme.
The second term on the right hand side of (V.12) and the third term on the right hand side of (V.17) are of relative order $k\, h(\zeta)$ compared to the first term.
By neglecting such terms in the hydrodynamic propagators $\tilde{G}_\eta(k,t)$, $\tilde{G}(k,t)$ occurring in (V.9) we obtain indeed (V.14,15,16) as the first approximation to U(k,z) and G(k,z) .

If we would have taken into account these terms in the hydrodynamic propagators one can also verify that such terms contribute corrections to $U(k,z)$ and $G(k,z)$ of relative order $k^2\ h(\zeta)$ compared to the leading term.
Therefore the perturbation expansion is consistent up to relative order $k^2\ h(\zeta)$.

In the following section we calculate (V.14,16) and we drop the superscripts (1) from now on.

b. Calculation of U(k,z) and G(k,z)

We start with $\Delta U(k,z)$ given in (V.14). Substitution of (V.17) yields for $\zeta = z/Dk^2$ finite

$$\cdot \quad \Delta U(k,z) = \frac{1}{\beta mn(2\pi)^3} \int' d\vec{q} \, \{ 1 - (\hat{k}.\hat{q})^2 \}$$

$$\left[\frac{e^{-(z+\nu q^2+Dl^2)t_o}}{z+\nu q^2+Dl^2} - \frac{e^{-(\nu+D)q^2t_o}}{(D+\nu)q^2} + \sum_{n=1}^{\infty} \Delta_\eta(n) \, q^{p_n} \right.$$

$$\left\{ \frac{q^2}{(z+\nu q^2+Dl^2)^2} (1+(z+\nu q^2+Dl^2)t_o) \, e^{-(z+\nu q^2+Dl^2)t_o} + \right.$$

$$\left. \left. - \frac{1+(D+\nu)q^2t_o}{(D+\nu)^2q^2} \, e^{-(D+\nu)q^2t_o} \right\} \right] \quad + O(k^2h(\zeta)) \, . \qquad \text{(V.21)}$$

We change to the appropriate hydrodynamic variables, such that the frequency z is measured in units k^{-2} .
It is convenient to define the dimensionless frequency s to be

$$\cdot \quad s \equiv \delta^{-1} \, (\, z/(Dk^2) + 1 \,) \, . \qquad \text{(V.22)}$$

Here the dimensionless quantity δ is defined as

$$\cdot \quad \delta \equiv D \, / \, (D+\nu) \, , \qquad \text{(V.23)}$$

where δ is a real number between zero and one.
Furthermore we will use in (V.21) the dimensionless integration variables $x = \hat{k}.\hat{q}$ and $y = q/(\delta k)$ and we define

$$\cdot \quad k^{*} \equiv 4\pi \, \beta mn \, D(D+\nu) \, , \qquad \text{(V.24)}$$

which has the dimension of an inverse microscopic length; and we define the quantities

$$\cdot \quad a_n \equiv \Delta_\eta(n)\, D^{-1}\, \delta^{1+p_n} \,, \qquad (n=1,2,\ldots) \qquad (V.25)$$

which have the dimension of a length to the power p_n .
All this is substituted into (V.21) and the $\vec{q}$ integral ($\sim$ x,y integral) is performed term by term. In each term the upperlimit $k_o/\delta k$ in the y integral is replaced by infinity and t_o is replaced by o . Roughly speaking this is allowed since $k \ll k_o$ and $z \ll z_o = t_o^{-1}$. More precisely, the errors made by doing so are at least of order $k^2\, h(s)$ and must be neglected consistently in (V.21). In this way we arrive at expressions for $\Delta U(k,z)$ and $U(k,z)$ of the final form

$$\cdot \quad U(k,z) = D + \Delta U(k,z) \qquad (V.26)$$

$$\cdot \quad \Delta U(k,z) = D\delta \frac{k}{k^*} u(s) + D\delta \frac{k}{k^*} \sum_{n=1}^{\infty} a_n\, k^{p_n}\, u_{p_n}(s) + O(k^2 h(s)) \,. \qquad (V.27)$$

The expansion (V.27) is valid for fixed values of s and values of k such that $Dk^2 t_o \ll \min\,(Dk_o^2 t_o, 1/s)$, as illustrated by the shaded area in figure 13a. This is a consequence of the requirements $k \ll k_o$, $z \ll z_o$ imposed on (V.8).
The functions $u(s)$ and $u_{p_n}(s)$ are at least analytic for Re $s > 1/\delta$, corresponding to Re $z > o^n$.
Explicit expressions for $u(s)$ and $u_p(s)$, with $o<p<1$, are obtained from (V.21) with the result

$$\cdot \quad u(s) = \pi^{-1} \int_o^\infty dy \int_{-1}^{+1} dx\, (1-x^2) \left[\frac{y^2}{s-2xy+y^2} - 1 \right] \qquad (V.28)$$

$$\cdot \quad u_p(s) = \pi^{-1} \int_o^\infty dy \int_{-1}^{+1} dx\, (1-x^2)\, y^p \left[\frac{y^4}{(s-2xy+y^2)^2} - 1 \right] \,. \qquad (V.29)$$

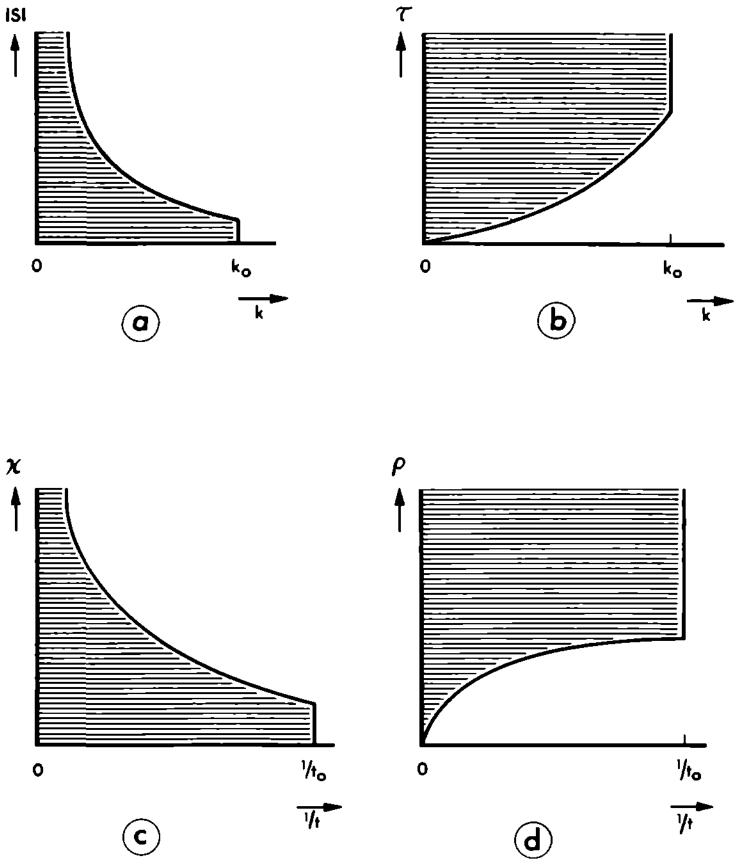

figure 13 : Regions of validity of the series expansions:
a for (V.27,39), b for (V.44,45), c for (V.49) and
d for (V,74,76).

The integrals in (V.28) and (V.29) are carried out in Appendix A with the result

$$\cdot \quad u(s) = -\frac{2}{3}\ \sqrt{s}\ \ {}_2F_1(\tfrac{3}{2},-\tfrac{1}{2};\tfrac{5}{2};\tfrac{1}{s}) \tag{V.30a}$$

$$= \frac{1}{4}\ (s-2)\ \sqrt{s-1} - \frac{1}{4}\ s^2\ \tan^{-1}\frac{1}{\sqrt{s-1}} \tag{V.30b}$$

$$\cdot \quad u_p(s) = -\frac{(3+p)\ s^{(1+p)/2}}{3\cos\frac{p\pi}{2}}\ {}_2F_1(\tfrac{5+p}{2},-\ \tfrac{1+p}{2};\tfrac{5}{2};\tfrac{1}{s}) \tag{V.31a}$$

$$= \frac{s^{(4+p)/2}}{2\cos\frac{p\pi}{2}}\ [\ \frac{1}{4+p}\sin\{\ (4+p)\ \tan^{-1}\frac{1}{\sqrt{s-1}}\ \} +$$

$$-\frac{1}{2+p}\sin\{\ (2+p)\ \tan^{-1}\frac{1}{\sqrt{s-1}}\ \}\ ]\ . \tag{V.31b}$$

Here ${}_2F_1(a,b;c;z)$ is Gauss' hypergeometric function (Erdelyi 1953). The presentation of our results in hypergeometric functions is very convenient in view of the inverse Laplace transforms to be carried out in the next section.

Properties of the hypergeometric function ${}_2F_1$, the confluent hypergeometric function ${}_1F_1(a;b;z)$ and the generalized hypergeometric functions ${}_pF_q(a_1,\ldots,a_p;b_1,\ldots,b_q;z)$, which we will need in this chapter, are given in reference (Erdelyi 1953). They are defined as

$$\cdot \quad {}_pF_q(a_1,\ldots,a_p;b_1,\ldots,b_q;z) = \sum_{n=o}^{\infty} \frac{(a_1)_n\ \ldots\ (a_p)_n}{(b_1)_n\ \ldots\ (b_q)_n}\frac{1}{n!}\ z^n\ , \tag{V.32}$$

where $(a)_n$ is Pochhammer's symbol

$$\cdot \quad (a)_n = a(a+1)\ \ldots\ (a+n-1) = \Gamma(a+n)\ /\ \Gamma(a)\ . \tag{V.33}$$

Integral representations and asymptotic expansions for large values of argument z are given extensively in reference (Luke 1969).

The result (V.30b) has also been obtained in reference (Bedeaux 1974). The singularities of $u(s)$ and $u_p(s)$ with largest Re s are square root branch points, located in $s=1$, where the functions behave as

$$\cdot \quad u(s) = -\frac{\pi}{8} - \frac{\pi}{4}(s-1) + \frac{2}{3}(s-1)^{3/2} + O((s-1)^2) \qquad (V.34)$$

$$\cdot \quad u_p(s) = \frac{3+p}{(2+p)(4+p)} \operatorname{tg}(p\pi/2) - \sqrt{s-1} + O(s-1) \; . \qquad (V.35)$$

The branch point $s=1$ corresponds to $z = -(1-\delta)Dk^2$ in the complex z plane. The functions are made unique by a cut in the complex s plane on the real s axis from $-\infty$ to 1. The behaviour of $u(s)$ and $u_p(s)$ for large values of s is easily obtained from (V.30a,31a) and (V.32)

$$\cdot \quad u(s) = -\frac{2}{3} s^{1/2} [\; 1 + O(s^{-1}) \;] \qquad (V.36)$$

$$\cdot \quad u_p(s) = -\frac{3+p}{3\cos(p\pi/2)} s^{(1+p)/2} [\; 1 + O(s^{-1}) \;] \; . \qquad (V.37)$$

The generalized diffusion coefficient $U(k,z)$ is now known up to order k^2 (for z/k^2 finite).

The *small* z behaviour of the Laplace transform of the velocity correlation function $C(z) = U(o,z)$ (I.67) is obtained from the behaviour of the functions $u(s)$ and $u_p(s)$ for *large* values of s (V.36,37). We choose a fixed value of $z \ll z_o$ and substitute in (V.27) $s = \delta^{-1}(z/(Dk^2)+1)$. Then the limit $k \to o$ of the expression (V.27) can be performed *within* its region of validity, yielding

$$\cdot \quad C(z) = D - \frac{1}{6\pi \, \beta mn \, (D+\nu)^{3/2}} z^{1/2} + $$

$$- \sum_{n=1}^{\infty} \frac{(3+p_n)\, \Delta_\eta(n)}{12\pi \, \beta mn \cos(p_n\pi/2)\, (D+\nu)^{(5+p_n)/2}} z^{(1+p_n)/2} + O(z) \; . \qquad (V.38)$$

We return to the velocity correlation function in the next section.

Let us now study $G(k,z)$ in first approximation.
By using again the variable s instead of z we find from (V.16) and (V.27) the series expansion

$$G(k,z) = \frac{1}{\delta D k^2 s} \left[1 - \frac{k}{k^{\star}} u(s)/s - \frac{k}{k^{\star}} \sum_{n=1}^{\infty} a_n k^{p_n} u_{p_n}(s)/s + O(k^2 h(s)) \right] \tag{V.39}$$

valid for fixed s and k such that $Dk^2 t_o \ll \min(Dk_o^2 t_o, 1/s)$, as illustrated by the shaded area in figure 13a.
The first term of this series expansion is just Fick's law prediction (I.35) (i.e. $G(k,z) \sim (z+Dk^2)^{-1}$ for $k \to o$ and $z/(Dk^2)$ fixed).

c. Calculation of $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$

Here we calculate the functions $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$ from the results of the previous section.
We start from

$$\tilde{U}(k,t) = \frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty} dz\ e^{zt}\ U(k,z) \qquad (V.40a)$$

$$\tilde{G}(k,t) = \frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty} dz\ e^{zt}\ G(k,z)\ , \qquad (V.40b)$$

where ϵ is a positive real number, and we study these functions for $k \ll k_o$, and large times.
As explained in chapter I we measure time in units k^{-2} and define therefore

$$\tau = Dk^2 t\ , \qquad (V.41)$$

so that the functions $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$ are expressed in the variables k and τ, instead of k and t . By introducing into (V.40) the integration variable $s = \delta^{-1}(z/Dk^2+1)$ we obtain

$$\tilde{U}(k,t) = \frac{\delta Dk^2}{2\pi i}\ e^{-\tau}\int_\Gamma ds\ e^{\delta s\tau}\ U(k,Dk^2(\delta s-1)) \qquad (V.42a)$$

$$\tilde{G}(k,t) = \frac{\delta Dk^2}{2\pi i}\ e^{-\tau}\int_\Gamma ds\ e^{\delta s\tau}\ G(k,Dk^2(\delta s-1))\ , \qquad (V.42b)$$

where the contour Γ runs through the complex s plane from $1+\epsilon-i\infty$ to $1+\epsilon+i\infty$.
Then we divide the s integral into two parts: $\int' ds$ (where $|s| < s_o \sim (Dk^2 t_o)^{-1}$, corresponding to $|z| < z_o$) and $\int'' ds$ (where $|s| > s_o$) . The basic assumption of the mode coupling theory was that it described

the dominant singularities of $\tilde{U}(k,t)$ for large t and of $U(k,z)$ for small z . Therefore we have to assume that the behaviour of $U(k,z)$ for large values of z ($z > z_o$) is irrelevant for the long time behaviour of $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$ and we omit the integrals $\int''$ ds in (V.42).
The expansions (V.27) and (V.39) for $\Delta U(k,z)$ and $G(k,z)$ may be inserted in $\int'$ ds , as can be seen from their domains of validity (figure 13a).
The s integrals are performed term by term, yielding expressions for $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$ of the final form

$$\tilde{U}(k,t) = D\,\delta(t) + \Delta\tilde{U}(k,t) \tag{V.43}$$

$$\Delta\tilde{U}(k,t) = \delta^2 D^2 k^2 \left[\frac{k}{k^*} e^{-\tau} \left\{ v(\delta\tau) + \sum_{n=1}^{\infty} a_n k^{p_n} v_{p_n}(\delta\tau) \right\} + O(k^2 h(\tau)) \right] \tag{V.44}$$

$$\tilde{G}(k,t) = e^{-\tau} \left[1 - \frac{k}{k^*} w(\delta\tau) - \frac{k}{k^*} \sum_{n=1}^{\infty} a_n k^{p_n} w_{p_n}(\delta\tau) + O(k^2 h(\tau)) \right] . \tag{V.45}$$

The first term in (V.43) represents the short time behaviour of $\tilde{U}(k,t)$.
The series expansions (V.44,45) are valid at fixed τ and values of k such that $Dk^2 t_o \ll \min(Dk_o^2 t_o, \tau)$, as illustrated by the shaded area in figure 13b.
The expansions (V.44,45) may equivalently be considered as expansions in the smallness parameter 1/t with coefficients, which are functions of the dimensionless wave number κ , defined as

$$\kappa = k\sqrt{Dt} . \tag{V.46}$$

We rewrite the expansions (V.44,45) with the help of (V.41), yielding

$$\Delta\tilde{U}(k,t) = \frac{\delta^2 D^2}{k^* (Dt)^{3/2}} \kappa^3 e^{-\kappa^2} \left\{ v(\delta\kappa^2) + \sum_{n=1}^{\infty} \frac{a_n}{(Dt)^{p_n/2}} \kappa^{p_n} v_{p_n}(\delta\kappa^2) \right\} + O(h(\kappa)/t^2) \tag{V.47}$$

$$\tilde{G}(k,t) = e^{-\kappa^2} \Big[1 - \frac{\kappa}{k^\star (Dt)^{1/2}} w(\delta\kappa^2) - \frac{\kappa}{k^\star (Dt)^{1/2}} \sum_{n=1}^{\infty} \frac{a_n}{(Dt)^{p_n/2}} \kappa^{p_n} w_{p_n}(\delta\kappa^2) \Big] + O(\frac{h(\kappa)}{t}) . \qquad (V.48)$$

These expansions are valid at fixed κ and t such that $t >> \max(t_o, \kappa^2/(Dk_o^2))$ as illustrated by the shaded area in figure 13c.
Note that the first term in (V.45) or (V.48) is Fick's law prediction (I.34).

Explicit relations for the functions v, v_p, w, w_p occurring (V.44, 45,47,48) are obtained from (V.42) and the series expansions (V.27,39), yielding

$$v(\tau) = \frac{1}{2\pi i} \int_{\Gamma}' ds\ e^{s\tau}\ u(s) \qquad (V.49)$$

$$v_p(\tau) = \frac{1}{2\pi i} \int_{\Gamma}' ds\ e^{s\tau}\ u_p(s) \qquad (V.50)$$

$$w(\tau) = \frac{1}{2\pi i} \int_{\Gamma}' ds\ e^{s\tau}\ u(s)/s^2 \qquad (V.51)$$

$$w_p(\tau) = \frac{1}{2\pi i} \int_{\Gamma}' ds\ e^{s\tau}\ u_p(s)/s^2 , \qquad (V.52)$$

where the integrals are restricted to $|s| < s_o \sim (Dk^2 t_o)^{-1}$.
It is clear from these relations that

$$v(\tau) = (\frac{\partial}{\partial\tau})^2\ w(\tau) \qquad (V.53)$$

$$v_p(\tau) = (\frac{\partial}{\partial\tau})^2\ w_p(\tau) . \qquad (V.54)$$

Strictly speaking the functions v, v_p, w, w_p as defined by (V.49-52) depend on τ *and* k , since the cut-off frequency s_o is a function of k . The k dependence of these functions is removed in the following way.

The asymptotic behaviour of $u(s)$ and $u_p(s)$ for large values of s is given in (V.36,37): $u(s) \sim s^{1/2}$ and $u_p(s) \sim s^{(1+p)/2}$. Therefore the upperlimit s_o in (V.51) and (V.52) may be replaced by ∞ and the resulting functions $w(\tau)$ and $w_p(\tau)$ are well defined (τ=o *included*).

The errors made in doing so are of order $k^2h(\tau)$ and must be neglected consistently in (V.45).

This result for $w(\tau)$ and $w_p(\tau)$ is substituted into (V.53,54) yielding the k independent functions $v(\tau)$ and $v_p(\tau)$.

It can be shown that $v(\tau)$ and $v_p(\tau)$ obtained in this way represent the functions $v(\tau)$ and $v_p(\tau)$ as defined by (V.49,50) up to order $k^2h(\tau)$, if k and τ are chosen inside the shaded area drawn in figure 13b with k=o , τ=o *excluded*.

We note that $w(\tau)$ and $w_p(\tau)$ resulting from this procedure may be considered as the inverse Laplace transforms of $u(s)/s^2$ and $u_p(s)/s^2$ respectively. The results for $v(\tau)$ and $v_p(\tau)$ are *not* the inverse Laplace transforms of $u(s)$ and $u_p(s)$.

To obtain explicit expressions for $w(\tau)$ and $w_p(\tau)$ we quote the inverse Laplace transform of the generalized hypergeometric function (Erdelyi 1954,1)

$$\frac{1}{2\pi i}\int_\Gamma ds\, e^{s\tau}\, s^{-\sigma}\, {}_pF_q(a_1,\dots,a_p;b_1,\dots,b_q;s^{-1}) =$$

$$(\Gamma(\sigma))^{-1}\,\tau^{\sigma-1}\,{}_pF_{q+1}(a_1,\dots,a_p;b_1,\dots,b_q,\sigma;\tau)\ , \qquad \text{(V.55)}$$

which is valid for $p \leqslant q+1$ and Re $\sigma > o$.

From this, (V.30a,31a) and (V.51,52), we find straightforwardly

$$w(\tau) = -\frac{4}{3\sqrt{\pi}}\,\tau^{1/2}\,{}_1F_1(-\tfrac{1}{2};\tfrac{5}{2};\tau) \qquad \text{(V.56)}$$

$$\cdot \quad w(\tau) = \frac{1}{4\sqrt{\pi}} \tau^{-1/2} e^{\tau} [\tau^{-1/2} F(\tau^{1/2}) \{ 4\tau^2 - 4\tau - 1 \} - 2\tau + 1] \quad (V.57)$$

$$\cdot \quad w_p(\tau) = \frac{-8\,\Gamma((5+p)/2)}{3\pi\,(1-p^2)} \tau^{(1-p)/2}\ {}_2F_2(\tfrac{5+p}{2}, -\tfrac{1+p}{2}; \tfrac{3-p}{2}, \tfrac{5}{2}; \tau) \,. \quad (V.58)$$

To obtain (V.56) we have used the property that ${}_pF_q$ reduces to ${}_{p-1}F_{q-1}$ if $a_i = b_j$ as can be seen easily from (V.32).

The result (V.56) can be expressed in terms of more elementary functions, as given in (V.57) by using simple properties of the confluent hypergeometric function ${}_1F_1$ and the relation (Abramowitz 1970)

$$\cdot \quad {}_1F_1(1;\tfrac{3}{2};-\tau) = \tau^{-1/2} F(\tau^{1/2}) \,, \quad (V.59)$$

where $F(x)$ is Dawson's integral, related to the error function as

$$\cdot \quad F(x) = \tfrac{1}{2}\sqrt{\pi}\ i \exp(-x^2) \operatorname{erf}(-ix) \,.$$

We note that the result (V.58) can not be expressed in elementary functions.

The functions $v(\tau)$ and $v_p(\tau)$ can now be calculated from (V.53,54) and from elementary relations for derivatives of generalized hypergeometric functions (Luke 1969) with the result

$$\cdot \quad v(\tau) = \frac{1}{3\sqrt{\pi}} \tau^{-3/2}\ {}_1F_1(\tfrac{3}{2};\tfrac{5}{2};\tau)$$

$$= \frac{1}{2\sqrt{\pi}} \tau^{-5/2} e^{\tau} \{ 1 - \tau^{-1/2} F(\tau^{1/2}) \} \quad (V.60)$$

$$\cdot \quad v_p(\tau) = \frac{2}{3\pi} \Gamma((5+p)/2)\, \tau^{-(3+p)/2}\ {}_1F_1(\tfrac{5+p}{2};\tfrac{5}{2};\tau) \,. \quad (V.61)$$

The small τ behaviour of v , v_p , w , w_p , is given by

. $$v(\tau) = \frac{1}{3\sqrt{\pi}}\,\tau^{-3/2}\ \{\ 1 + O(\tau)\ \} \qquad \text{(V.62)}$$

. $$v_p(\tau) = \frac{2}{3\pi}\,\Gamma((5+p)/2)\ \tau^{-(3+p)/2}\ \{\ 1 + O(\tau)\ \} \qquad \text{(V.63)}$$

. $$w(\tau) = -\frac{4}{3\sqrt{\pi}}\,\tau^{1/2}\ \{\ 1 + O(\tau)\ \} \qquad \text{(V.64)}$$

. $$w_p(\tau) = -\frac{8\,\Gamma((5+p)/2)}{3\pi\ (1-p^2)}\,\tau^{(1-p)/2}\ \{\ 1 + O(\tau)\ \}\ . \qquad \text{(V.65)}$$

We note here that $v(\tau)$ and $v_p(\tau)$ diverge as $\tau \to o$, therefore the Laplace transform of these functions does not exist, as was mentioned above. For large values of τ asymptotic series expansions for ${}_1F_1$ and ${}_2F_2$ are given in reference (Luke 1969), yielding

. $$v(\tau) = \frac{1}{2\sqrt{\pi}}\,e^{\tau}\ \tau^{-5/2}\ \{\ 1 + O(\tau^{-1})\ \} \qquad \text{(V.66)}$$

. $$v_p(\tau) = \frac{1}{2\sqrt{\pi}}\,e^{\tau}\ \tau^{-3/2}\ \{\ 1 + O(\tau^{-1})\ \} \qquad \text{(V.67)}$$

. $$w(\tau) = \frac{1}{2\sqrt{\pi}}\,e^{\tau}\ \tau^{-5/2}\ \{\ 1 + O(\tau^{-1})\ \} \qquad \text{(V.68)}$$

. $$w_p(\tau) = \frac{1}{2\sqrt{\pi}}\,e^{\tau}\ \tau^{-3/2}\ \{\ 1 + O(\tau^{-1})\ \}\ . \qquad \text{(V.69)}$$

Finally in this section we study the large time behaviour of the velocity correlation function $\tilde{C}(t) = \tilde{U}(o,t)$ from (I.68).
Choose a fixed time $t \gg t_o$, and substitute $\tau = Dk^2 t$ in (V.44).
Then the limit $k \to o$ of this expression can be performed at fixed values of t , staying inside the range of validity of (V.44) (see figure 13b).
This yields for $t \gg t_o$

. $$\tilde{C}(t) = D\,\delta(t) + \frac{1}{12\,\pi^{3/2}\ \beta mn\ (D+\nu)^{3/2}}\,\frac{1}{t^{3/2}}\ \{\ 1 +$$

$$\sum_{n=1}^{\infty} \frac{2\,\Gamma((5+p_n)/2)\,\Delta_\eta(n)}{\pi^{1/2}\,(D+\nu)^{(2+p_n)/2}}\,\frac{1}{t^{p_n/2}}\,\Big\} + O\Big(\frac{1}{t^2}\Big) \qquad (V.70)$$

We note that the *large* time behaviour of $\tilde{C}(t)$ is obtained from the *small* τ behaviour of $v(\tau)$ and $v_p(\tau)$ given in (V.62,63).

The result (V.70) has first been given in reference (Ernst 1974).

d. Calculation of $\tilde{\tilde{U}}(r,t)$ and $\tilde{\tilde{G}}(r,t)$

Here the predictions from the mode coupling theory are calculated for the functions $\tilde{\tilde{U}}(\vec{r},t)$ and $\tilde{\tilde{G}}(\vec{r},t)$, where $\tilde{\tilde{G}}(\vec{r},t)$ is defined in (I.13) and $\tilde{\tilde{U}}(\vec{r},t)$ is defined as the inverse Fourier transform of $\tilde{U}(\vec{k},t)$ in (I.59).
As explained in chapter I we use the variables $\vec{\rho}$ and t instead of $\vec{r}$ and t to describe these functions, where $\vec{\rho}$ is defined as

$$\vec{\rho} = \vec{r} \,/\, \sqrt{Dt} \,. \tag{V.71}$$

For fixed values of ρ the inverse time $1/t$ is used as small parameter ($1/t \ll 1/t_o$) , to obtain expansions beyond the lowest order Fick's law prediction (I.33).
We start from the relations

$$\tilde{\tilde{U}}(\vec{r},t) = (2\pi)^{-3} \int d\vec{k}\; e^{i\vec{k}.\vec{r}}\, \tilde{U}(\vec{k},t) \tag{V.72}$$

$$\tilde{\tilde{G}}(\vec{r},t) = (2\pi)^{-3} \int d\vec{k}\; e^{i\vec{k}.\vec{r}}\, \tilde{G}(\vec{k},t) \,. \tag{V.73}$$

The parameters $\vec{\rho}$ and t are substituted in these expressions and the integration variable $\vec{k}$ is changed into $(x,\hat{k})$ where $x = k\sqrt{Dt}$ (compare (V.46), so that $x = \kappa$) . The resulting x integrals are divided into two parts $\int' dx$, where $x < k_o\sqrt{Dt}$ (corresponding to $k < k_o$) and $\int'' dx$ where $x > k_o\sqrt{Dt}$. The integrals $\int'' dx$ involve the functions $\tilde{U}(k,t)$ and $\tilde{G}(k,t)$ for values of k larger than k_o .
As an illustration we consider $\tilde{U}(k,t)$ for large k .
For distances much smaller than k_o^{-1} the interactions between the particles may be neglected and the correlation function $\tilde{U}(k,t)$ behaves as in an ideal gas

$$\tilde{U}(k,t) \sim \exp(-k^2t^2/(2\beta m)). \qquad (k \gg k_o)$$

Using this relation for all $k > k_o$, the contribution to $\tilde{\tilde{U}}(r,t)$ arising from the integral $\int'' dx$ decays at least as fast as

$$\tilde{\tilde{U}}''(r,t) \sim \frac{4\pi}{r} \int_{k_o}^{\infty} dk\, k \exp\{-k^2 t^2/(2\beta m)\} \sim \frac{1}{\rho t^{5/2}} e^{-\alpha t^2}$$

at fixed values of ρ. Such contributions to $\tilde{\tilde{U}}(r,t)$ may be neglected as we will see below.

In general it is assumed here that at fixed values of ρ the contributions to $\tilde{\tilde{U}}(r,t)$ and $\tilde{\tilde{G}}(r,t)$ arising from the integrals $\int'' dx$ in (V.72, 73) (i.e. $k > k_o$) are at least of order $(1/t)^{7/2}$ for $\tilde{\tilde{U}}(r,t)$ or $(1/t)^{5/2}$ for $\tilde{\tilde{G}}(r,t)$.

As the next step the series expansions (V.43,47) for $\tilde{U}(k,t)$ and (V.48) for $\tilde{G}(k,t)$ are inserted in the term $\int' dx$ in (V.72,73). This is allowed since the upperlimit is of order $k_o \sqrt{Dt}$, so that the requirements on the expansions (V.47) and (V.48) are satisfied.
Next we replace the upperlimit by infinity, which introduces corrections to $\tilde{\tilde{U}}$ and $\tilde{\tilde{G}}$ which are, at fixed ρ proportional to $\exp(-Dk_o^2 t)$.
The resulting expressions are only meaningful for values of ρ such that $\rho^{-1} < k_o \sqrt{Dt}$. In this way we arrive at expressions for $\tilde{\tilde{G}}(r,t)$ and $\tilde{\tilde{U}}(r,t)$ of the final form

$$\tilde{\tilde{G}}(r,t) = \frac{e^{-\rho^2/4}}{(4\pi Dt)^{3/2}} [\ 1 - \frac{1}{k^\star\ (Dt)^{1/2}} g(\rho) + $$

$$- \frac{1}{k^\star\ (Dt)^{1/2}} \sum_{n=1}^{\infty} \frac{a_n}{(Dt)^{p_n/2}} g_{p_n}(\rho) + O(\frac{h(\rho)}{t})\ ] \tag{V.74}$$

and

$$\tilde{\tilde{U}}(\vec{r},t) = D\, \delta(\vec{r})\, \delta(t) + \Delta\tilde{\tilde{U}}(\vec{r},t) \tag{V.75}$$

with

$$\cdot \quad \Delta\tilde{\tilde{U}}(r,t) = \frac{\delta^2 \, e^{-\rho^2/4}}{8\pi^{3/2} \, Dk^{\ast} \, t^3} [\; f(\rho) +$$

$$+ \sum_{n=1}^{\infty} \frac{a_n}{(Dt)^{p_n/2}} f_{p_n}(\rho) + O(\frac{h(\rho)}{\sqrt{t}}) \;] \; . \qquad (V.76)$$

The series expansions (V.74,76) are valid for fixed values of ρ and for times t such that $t \gg \max(t_o,(Dk_o^2 \, \rho^2)^{-1})$, as illustrated by the shaded area in figure 13d. The first term in (V.74) represents Fick's law prediction (I.33).

The functions $g(\rho)$, $g_p(\rho)$, $f(\rho)$ and $f_p(\rho)$ are given by

$$\cdot \quad g(\rho) = \frac{4 \, e^{\rho^2/4}}{\sqrt{\pi} \, \rho} \int_0^{\infty} dx \, \sin(x\rho) \, x^2 \, e^{-x^2} \, w(\delta x^2) \qquad (V.77)$$

$$\cdot \quad g_p(\rho) = \frac{4 \, e^{\rho^2/4}}{\sqrt{\pi} \, \rho} \int_0^{\infty} dx \, \sin(x\rho) \, x^{2+p} \, e^{-x^2} \, w_p(\delta x^2) \qquad (V.78)$$

$$\cdot \quad f(\rho) = \frac{4 \, e^{\rho^2/4}}{\sqrt{\pi} \, \rho} \int_0^{\infty} dx \, \sin(x\rho) \, x^4 \, e^{-x^2} \, v(\delta x^2) \qquad (V.79)$$

$$\cdot \quad f_p(\rho) = \frac{4 \, e^{\rho^2/4}}{\sqrt{\pi} \, \rho} \int_0^{\infty} dx \, \sin(x\rho) \, x^{4+p} \, e^{-x^2} \, v_p(\delta x^2) \; . \qquad (V.80)$$

The functions $g(\rho)$ and $g_p(\rho)$ are calculated in appendix B, with the result

$$\cdot \quad g(\rho) = -2 \, \{\frac{1-\delta}{\pi\delta}\}^{\frac{1}{2}} \, \{ \; {}_1F_1(-\tfrac{1}{2};\tfrac{3}{2};-\frac{\delta\rho^2}{4(1-\delta)}) +$$

$$- \, (1-\delta) \; {}_1F_1(-\tfrac{3}{2};\tfrac{3}{2};-\frac{\delta\rho^2}{4(1-\delta)}) \; \} \; . \qquad (V.81)$$

$$g(\rho) = \frac{1}{4} \left\{\frac{1-\delta}{\pi\delta}\right\}^{\frac{1}{2}} \left[(1-5\delta+\tfrac{1}{2}\delta\rho^2) \exp\left(-\frac{\delta\rho^2}{4(1-\delta)}\right) + \right.$$

$$\left. + \frac{\sqrt{\pi}}{\sqrt{\delta(1-\delta)}\,\rho} \operatorname{erf}\left(\sqrt{\frac{\delta\rho^2}{4(1-\delta)}}\right) \{ -(1-\delta)(1+3\delta) + (1-3\delta)\delta\rho^2 + \tfrac{1}{4}\delta^2\rho^4 \} \right] . \tag{V.82}$$

Equation (V.81) is expressed in more elementary functions (V.82) by means of elementary properties of ${}_1F_1$ and the relation (Abramowitz 1970)

$$\operatorname{erf}(x) = 2\,\pi^{-\frac{1}{2}}\, x\; {}_1F_1(\tfrac{1}{2};\tfrac{3}{2};-x^2) .$$

For $g_p(\rho)$ we obtained in appendix B a hypergeometric series of two variables, δ and $\delta\rho^2/4$ respectively, which can also be written as a series expansion in powers of ρ

$$g_p(\rho) = -\frac{4\,\Gamma((5+p)/2)\,\delta^{(1-p)/2}}{\pi\,(1-p^2)} \sum_{m=o}^{\infty} \frac{(\frac{5+p}{2})_m\,(-\frac{1+p}{2})_m}{(\frac{3-p}{2})_m\,(\frac{3}{2})_m\, m!}$$

$$ {}_2F_1(m+\tfrac{5+p}{2}, m-\tfrac{1+p}{2}; m+\tfrac{3-p}{2};\delta)\, \left\{1-\frac{\rho^2}{4m+6}\right\} \left\{\frac{-\delta\rho^2}{4}\right\}^m . \tag{V.83}$$

The functions $f(\rho)$ and $f_p(\rho)$ are hypergeometric series in two variables, δ and $\delta\rho^2/4$, which converges absolutely in the whole complex ρ plane. This result, and asymptotic expansions, can be obtained by the same method as used in appendix B for $g_p(\rho)$. We only quote the results

$$f(\rho) = \frac{1}{3\sqrt{\pi}}\,\delta^{-3/2}\, I(\tfrac{3}{2};\rho) \tag{V.84}$$

$$f_p(\rho) = \frac{2\,\Gamma((5+p)/2)}{3\pi}\,\delta^{-(3+p)/2}\, I(\tfrac{5+p}{2};\rho) , \tag{V.85}$$

where $I(a;\rho)$ can be written as a series in ρ^2 ,

$$\cdot \quad I(a;\rho) = \sum_{n=0}^{\infty} {}_2F_1(a+n,\tfrac{3}{2}+n;\tfrac{5}{2}+n;\delta)\,\frac{(a)_n}{(\frac{5}{2})_n\; n!}\,\{-\frac{\delta\rho^2}{4}\}^n\,. \tag{V.86}$$

The small ρ behaviour of $g(\rho)$, $g_p(\rho)$, $f(\rho)$ and $f_p(\rho)$ is given by

$$\cdot \quad g(\rho) = -\,2\sqrt{\frac{\delta(1-\delta)}{\pi}} + O(\rho^2) \tag{V.87}$$

$$\cdot \quad g_p(\rho) = -\,\frac{4\,\Gamma((5+p)/2)\,\delta^{(1-p)/2}}{\pi\,(1-p^2)}\;{}_2F_1(\tfrac{5+p}{2},-\tfrac{1+p}{2};\tfrac{3-p}{2};\delta) + O(\rho^2) \tag{V.88}$$

$$\cdot \quad f(\rho) = \frac{\delta^{-3/2}}{3\sqrt{\pi}}\;{}_2F_1(\tfrac{3}{2},\tfrac{3}{2};\tfrac{5}{2};\delta) + O(\rho^2) = \frac{\delta^{-3}}{\sqrt{\pi}}\{\,\frac{\sqrt{\delta}}{1-\delta} - \sin^{-1}\sqrt{\delta}\,\} + O(\rho^2) \tag{V.89}$$

$$\cdot \quad f_p(\rho) = \frac{2}{3\pi}\,\Gamma((5+p)/2)\;\delta^{-(3+p)/2}\;{}_2F_1(\tfrac{5+p}{2},\tfrac{3}{2};\tfrac{5}{2};\delta) + O(\rho^2)\,. \tag{V.90}$$

The behaviour of $g(\rho)$, $g_p(\rho)$, $f(\rho)$ and $f_p(\rho)$ for large values of ρ is given by asymptotic series expansions and we quote only the first terms

$$\cdot \quad g(\rho) = \frac{1}{16}\,\delta\,\rho^3\,[\;1 + O(\rho^{-2})\;] \tag{V.91}$$

$$\cdot \quad g_p(\rho) = \frac{\delta}{2(4+p)\cos(p\pi/2)}\,\rho^{3+p}\,[\;1 + O(\rho^{-2})\;] \tag{V.92}$$

$$\cdot \quad f(\rho) = 2\,\delta^{-3}\,\rho^{-3}\,[\;1 + O(\rho^{-2})\;] \tag{V.93}$$

$$\cdot \quad f_p(\rho) = -\,\frac{4}{\pi}\,(3+p)\,\Gamma(2+p)\,\sin(p\pi/2)\,\delta^{-4-p}\,\rho^{-5-p}\,[\;1 + O(\rho^{-2})\;]\,. \tag{V.94}$$

Pomeau (Pomeau 1972) has reported some results for the fluid propagators $\approx{G}_\lambda(r,t)$, which have some resemblance to our expression (V.74) for $\approx{G}(r,t)$. However in general the structure of G_λ and G differ considerably as one can see from (V.17) and (V.39).

e. Moments of displacement and related quantities.

In this section we calculate the predictions from mode coupling theory for the moments of displacement $M^{(n)}(t)$, defined in (I.36), the cumulants $M_c^{(n)}(t)$, defined in (I.40) and the time dependent diffusion coefficients $D^{(n)}(t)$ defined in (I.32).

Expressions for $M^{(n)}(t)$ are obtained from the relation (I.38a) and the result (V.45) for $\tilde{G}(k,t)$.
We choose a fixed time $t \gg t_o$, so that $\tau = Dk^2t \gg Dk^2t_o$. For all values of $k \ll k_o$ the parameter τ is inside the shaded area of figure 13b and the result (V.45) may be substituted into (I.38a). This yields with $x = \delta\tau$ and $j = 0,1,2,\ldots$

$$\cdot \quad M^{(2j)}(t) = (-)^j \frac{(2j)!}{j!} (\delta Dt)^j \lim_{x\to o} \left(\frac{\partial}{\partial x}\right)^j e^{-x/\delta}$$

$$\left[1 - \frac{x^{\frac{1}{2}} w(x)}{k^{\star} (\delta Dt)^{\frac{1}{2}}} - \sum_{n=1}^{\infty} \frac{a_n}{k^{\star} (\delta Dt)^{(1+p_n)/2}} x^{(1+p_n)/2} w_{p_n}(x) + O\left(\frac{h(x)}{t}\right) \right] . \qquad (V.95)$$

From this one obtains a series expansion for $M^{(2j)}(t)$ of the form

$$\cdot \ M^{(2j)}(t) = \frac{(2j)!}{j!} (Dt)^j \left[1 - \frac{m^{(j)}}{k^{\star} (Dt)^{\frac{1}{2}}} - \sum_{n=1}^{\infty} \frac{a_n}{k^{\star} (Dt)^{(1+p_n)/2}} m_{p_n}^{(j)} + O\left(\frac{1}{t}\right) \right] \qquad (V.96)$$

valid for t much larger than t_o and $j = 0,1,\ldots$.
The first term in (V.96) is Fick's law prediction (I.39).
The dimensionless numbers $m^{(j)}$ and $m_p^{(j)}$ are given by

$$\cdot \quad m^{(j)} = \delta^{j-\frac{1}{2}} \lim_{x\to o} \left(- \frac{\partial}{\partial x}\right)^j e^{-x/\delta} x^{\frac{1}{2}} w(x) \qquad (V.97)$$

$$m_p^{(j)} = \delta^{j-(1+p)/2} \lim_{x\to o} \left(-\frac{\partial}{\partial x}\right)^j e^{-x/\delta}\, x^{(1+p)/2}\, w_p(x) \; . \tag{V.98}$$

By substitution of the explicit expressions (V.56) and (V.58) for $w(x)$ and $w_p(x)$ and using the series expansion (V.32) for hypergeometric functions one finds straightforwardly

$$m^{(j)} = \frac{4j\,\delta^{\frac{1}{2}}}{3\sqrt{\pi}}\; {}_2F_1(-j+1,-\tfrac{1}{2};\tfrac{5}{2};\delta) \tag{V.99}$$

$$m_p^{(j)} = \frac{8j\,\Gamma((5+p)/2)\,\delta^{(1-p)/2}}{3\pi(1-p^2)}\; {}_3F_2(-j+1,\tfrac{5+p}{2},-\tfrac{1+p}{2};\tfrac{5}{2},\tfrac{3-p}{2};\delta)\;. \tag{V.100}$$

In these expressions ${}_2F_1(\ldots;\delta)$ and ${}_3F_2(\ldots;\delta)$ are polynomials in δ of degree $j-1$. This follows from (V.32) and the property $(-j+1)_n = o$ if $n > j$.
For $j = o$ we have $m^{(o)} = o$ and $m_p^{(o)} = o$, which is consistent with the property $M^{(o)}(t) = 1$ for all t , as follows from (I.36).
For $j = 1$ the polynomials ${}_2F_1(\ldots;\delta)$ and ${}_3F_2(\ldots;\delta)$ in (V.99,100) are equal to 1 , so that the second moment of displacement is given by

$$M^{(2)}(t) = 2Dt\,\Big[\;1 - \frac{1}{3\pi^{3/2}\,\beta mn\, D(D+\nu)^{3/2}\, t^{1/2}} + $$

$$- \frac{2}{3\pi^2\,\beta mn\, D} \sum_{n=1}^{\infty} \frac{\Gamma((5+p_n)/2)\;\Delta_\eta(n)}{(1-p_n^2)\;(D+\nu)^{(5+p_n)/2}\; t^{(1+p_n)/2}} + O(\tfrac{1}{t})\;\Big] \;, \tag{V.101}$$

where we have used the relations (V.23), (V.24) and (V.25) for δ , k^* and a_n .
The time dependent diffusion coefficient $D^{(o)}(t)$ defined in (I.32) is related to $M^{(2)}(t)$ by $D^{(o)}(t) = \frac{1}{2}\,(\partial/\partial t)\, M^{(2)}(t)$, as follows from (I.44) and (I.42). For $t \gg t_o$ we find therefore

$$D^{(o)}(t) = D\,\Big[\;1 - \frac{1}{6\pi^{3/2}\,\beta mn\, D(D+\nu)^{3/2}\, t^{1/2}} +$$

$$- \frac{1}{3\pi^2 \beta mn D} \sum_{n=1}^{\infty} \frac{\Gamma((5+p_n)/2)\, \Delta_\eta(n)}{(1+p_n)\,(D+\nu)^{(5+p_n)/2}\, t^{(1+p_n)/2}} + O(\tfrac{1}{t}) \;] \quad . \tag{V.102}$$

The velocity correlation function $\tilde{C}(t)$ can be obtained from this expression by using (I.45): $\tilde{C}(t) = (\partial/\partial t)\, D^{(o)}(t)$. This yields a result for $\tilde{C}(t)$, given already in (V.70).
The low density limit of the expression (V.102) for $D^{(o)}(t)$ has also been obtained in chapter III (III.24b) from kinetic theory.

Next we study the mode coupling prediction for the cumulants $M_c^{(n)}(t)$ defined in (I.40). Choosing a fixed time $t >> t_o$, the result (V.45) for $\tilde{G}(k,t)$ may be substituted in the expression (I.41) for $M_c^{(2j)}(t)$.
For $j = 1$ we use the relation (I.42): $M_c^{(2)}(t) = M^{(2)}(t)$, where the prediction for $M^{(2)}(t)$ is given by (V.101).
Series expansions for the higher cumulants are obtained from (I.41) and (V.45) by writing $\log\{e^{-\tau}(1-\epsilon)\} = -\tau - \epsilon + O(\epsilon^2)$, where ϵ represents the terms in (V.45), which are at least of order k , at fixed values of τ . The result for $t >> t_o$ and $j \geqslant 2$ is

$$\cdot \quad M_c^{(2j)}(t) = \frac{(2j)!}{j!} (Dt)^j \,[\; - \frac{q^{(j)}}{k^{*}\,(Dt)^{\frac{1}{2}}} - \sum_{n=1}^{\infty} \frac{a_n}{k^{*}\,(Dt)^{(1+p_n)/2}}\, q_{p_n}^{(j)} + O(\tfrac{1}{t}) \;]. \tag{V.103}$$

The dimensionless numbers $q^{(j)}$ and $q_p^{(j)}$ are determined from the relations

$$\cdot \quad q^{(j)} = (-)^j\, \delta^{\,j-\frac{1}{2}} \lim_{x\to o} (\frac{\partial}{\partial x})^j\, x^{\frac{1}{2}}\, w(x) \tag{V.104}$$

$$\cdot \quad q_p^{(j)} = (-)^j\, \delta^{\,j-(1+p)/2} \lim_{x\to o} (\frac{\partial}{\partial x})^j\, x^{(1+p)/2}\, w_p(x) \;. \tag{V.105}$$

By substitution of the expressions (V.56) and (V.58) for $w(x)$ and $w_p(x)$ one obtains

$$q^{(j)} = (-)^j \frac{4j\ \delta^{j-\frac{1}{2}}}{\sqrt{\pi}\ (2j+1)\ (2j-1)\ (2j-3)} \tag{V.106}$$

$$q_p^{(j)} = (-)^j \frac{2j\ \Gamma(j+(3+p)/2)\ \delta^{j-(1+p)/2}}{\sqrt{\pi}\ (2j-1-p)\ (2j-3-p)\ \Gamma(j+3/2)} \ . \tag{V.107}$$

It is obvious by comparing the expressions (V.97,98) and (V.104,105) that $q^{(j)}$ and $q_p^{(j)}$ are just equal to the terms in the polynomials $m^{(j)}$ and $m_p^{(j)}$ respectively, of highest degree in δ .

Expressions for the time dependent diffusion coefficients $D^{(2j)}(t)$ defined in (I.32) are obtained from (I.44) and (V.103). The result for $t \gg t_o$ and $j = 1,2,\ldots$ is

$$D^{(2j)}(t) = \frac{(-)^j}{2\pi^{3/2}\ (2j-1)\ (2j+3)\ j!} \ \frac{D^{2j}}{\beta mn\ (D+\nu)^{j+3/2}}\ t^{j-\frac{1}{2}}$$

$$\left[\ 1 + \sum_{n=1}^{\infty} \frac{(2j-1)\ \Gamma(j+(5+p_n)/2)}{(2j-1-p_n)\ \Gamma(j+3/2)} \ \frac{\Delta_\eta(n)}{(D+\nu)^{1+p_n/2}}\ t^{-p_n/2} + O(t^{-\frac{1}{2}})\ \right] \ . \tag{V.108}$$

The time dependent super Burnett coefficient is obtained from this expression by taking $j = 1$ so that

$$D^{(2)}(t) = - \frac{D^2}{10\pi^{3/2}\ \beta mn\ (D+\nu)^{5/2}}\ t^{\frac{1}{2}} \left[\ 1 + \right.$$

$$\left. + \sum_{n=1}^{\infty} \frac{4\ \Gamma((7+p_n)/2)}{3\ \sqrt{\pi}\ (1-p_n)} \ \frac{\Delta_\eta(n)}{(D+\nu)^{1+p_n/2}}\ t^{-p_n/2} + O(t^{-\frac{1}{2}})\ \right] \ . \tag{V.109}$$

The low density limit of this expression has also been obtained in chapter III (III.55) from kinetic theory.

f. Discussion

In this section we summarize a number of problems, which occur in the mode coupling theory presented in this chapter. They are a consequence of the fact that the mode coupling equation (V.1) is a priori restricted to small wave numbers ($k \ll k_o$) and large times ($t \gg t_o$) and even then it is only an asymptotic relation. Therefore the predictions from the mode coupling theory for the functions of interest in the diffusion problem $U(k,z)$, $G(k,z)$, $\tilde{U}(k,t)$, $\tilde{G}(k,t)$, $\tilde{\tilde{U}}(r,t)$ and $\tilde{\tilde{G}}(r,t)$ can only have any significance in the (hydrodynamic) regions $\{k<k_o;z<z_o \sim t_o^{-1}\}$, $\{k<k_o;t>t_o\}$ and $\{r>r_o \sim k_o^{-1};t>t_o\}$ respectively. However, to transform the mode coupling predictions from one language to another one, these functions are needed for all values of their arguments.

The first problem arises in finding, from a unified point of view, the weakest conditions for these functions outside the hydrodynamic regions, such that the transformations can actually be performed. The verification of such conditions is outside the scope of the mode coupling theory.

We partially considered this problem, e.g. in the transformation of $\tilde{U}(k,t)$ to $\tilde{\tilde{U}}(r,t)$ (compare (V.72-76)) where we discussed the plausibility that the contributions to $\tilde{\tilde{U}}(r,t)$ arising from $\tilde{U}(k,t)$ for large values of k do not interfere with the mode coupling predictions for $\tilde{U}(k,t)$, which are present for small values of k .

This property is assumed to be generally valid, however a detailed study of this point is still lacking.

Next we consider the functions U and G inside the hydrodynamic regions. The basic idea, which appears in the mode coupling theory, is that $\tilde{U}(k,t)$ and $U(k,z)$, (and eventually the other functions of interest) can be written as

$$\tilde{U}(k,t) = \tilde{U}_b(k,t) + \tilde{U}_m(k,t) \qquad \text{(V.110)}$$

and

$$U(k,z) = U_b(k,z) + U_m(k,z) \ , \qquad \text{(V.111)}$$

where $\tilde{U}_m(k,t)$ follows from the mode coupling equation (V.1) and is considered to be an asymptotic representation of $\tilde{U}(k,t)$ for large values of t ($t >> t_o$) and small values of k ($k << k_o$). The bare correlation function $\tilde{U}_b(k,t)$ is assumed to be less dominant in time for such values of k and t .

Equivalently $U_m(k,z)$ may be considered as an asymptotic representation of $U(k,z)$, which follows from the equation (V.8), and then the bare diffusion coefficient $U_b(k,z)$ is a less singular function than $U_m(k,z)$, for small values of k and z .

We note two difficulties related to the decompositions (V.110) and (V.111) for $\tilde{U}(k,t)$ and $U(k,z)$:

- There is no clear definition for $\tilde{U}_m(k,t)$ if $t < t_o$ and for $U_m(k,z)$ if $z < z_o$.
- The mode coupling equations (V.1) for $\tilde{U}_m(k,t)$ and (V.8) for $U_m(k,z)$ contain an adjustable parameter k_o (or a closely related cut-off time t_o) about which the theory does not make any explicit prediction.

The choice of a cut-off wave number k_o , the choice of $\tilde{U}_m(k,t)$ for $t < t_o$, or the choice of $U_m(k,z)$ for $z > z_o$, is to a certain extend arbitrary. Different choices for these quantities imply that less singular terms are shifted between $\tilde{U}_b(k,t)$ and $\tilde{U}_m(k,t)$ in (V.110) or between $U_b(k,z)$ and $U_m(k,z)$ in (V.111).

Therefore the decompositions (V.110,111) are not unique and this fact imposes a restriction on the mode coupling theory, since the theory does not make any prediction about the bare correlation functions

$\tilde{U}_b(k,t)$ or $U_b(k,z)$.

For this reason it is meaningless to define $U_m(k,z)$ as the exact Laplace transform of $\tilde{U}_m(k,t)$ (for some choice of $\tilde{U}_m(k,t)$ for $t < t_o$). It is meaningful only to say that $U_m(k,z)$ describes the asymptotic behaviour of $\tilde{U}_m(k,t)$ for large t .

Inversely it makes no sense to define $\tilde{U}_m(k,t)$ as the exact inverse Laplace transform of $U_m(k,z)$. It is sufficient that $\tilde{U}_m(k,t)$ contains the leading singularities of $U_m(k,z)$ for small z .

In this chapter we have introduced a perturbative scheme to solve the mode coupling equations, where the quantity $\Delta U(k,z) = U(k,z) - U(o,o)$ was used as the small parameter.

In that way we found in section *b* an expression for $\Delta U(k,z)$ of the form (V.21) and we have argued that this expression can be reduced to the form (V.27), which represents the mode coupling prediction for the leading singularities of $U(k,z)$.

To obtain the result (V.27) for $U(k,z)$ we implicitly used our basic assumption that the bare diffusion coefficient $U_b(k,z)$ is such that $\Delta U_b(k,z) = U_b(k,z) - U_b(o,o) \sim k^2 h(\zeta)$, so that $\Delta U_m(k,z)$ and $\Delta U(k,z)$ may be identified up to this order, and the singularities are indeed described by the mode coupling theory.

In section *c* we derived the leading singularities of $\tilde{U}(k,t)$ as expressed by (V.43,44) from the relation (V.27) for $U(k,z)$. As was mentioned already in the derivation, the result (V.43,44) is not trivially obtained by taking the inverse Laplace transform of (V.27) term by term. We review the derivation here.

The s integrals in (V.42) were divided into two parts $|s| < s_o$ (corresponding to $z < z_o$) and $|s| > s_o$. According to the arguments above the integrals involving values of s with $|s| > s_o$ are neglected. In the integrand of the integrals with $|s| < s_o$ the mode coupling prediction for $U(k,z)$ is inserted, and the integrals are performed term by term. Finally we removed the constraint $|s| < s_o$, and ob-

tained the result (V.43,44) for $\tilde{U}(k,t)$.
In particular the last point is not a trivial step, and we only have verified that it is allowed for the terms under consideration in (V.44). However this procedure imposes a restriction on the function h(s) in the correction term of order $k^2h(s)$ in (V.27), namely that

$$\cdot \quad \int_{s<(Dk^2t_o)^{-1}} ds\ e^{(\delta s-1)\tau}\ h(s)$$

is a well defined function of τ for $k\to o$.
More generally in the transformations of the mode coupling predictions from one language to another one, some global properties of the correction terms are needed, which we have not studied in detail here. Such a study would involve a more complete knowledge of the structure of the correction term of relative order $k^2h(\zeta)$ in the fluid propagator (V.12), and it would involve the second order approximation $\Delta U^{(2)}(k,z)$ to $\Delta U(k,z)$ (compare the discussion below (V.20)), which also gives terms of relative order $k^2h(\zeta)$.

As an illustration of this problem we consider the moments of displacement $M^{(n)}(t)$, which can be obtained from $\tilde{\tilde{G}}(r,t)$ by means of the relation (I.38b). The r integral may be divided into two parts $r < r_o$ and $r > r_o$, where the first part may be neglected as far as the mode coupling predictions are concerned. In the second part one may use the scaled integration variable $\rho = r/\sqrt{Dt}$ and the result (V.74) for $\tilde{\tilde{G}}(r,t)$ can be inserted.
By replacing the lower limit in the ρ integral, $r_o/\sqrt{Dt}$, by zero, one recovers the mode coupling prediction (V.96) for $M^{(n)}(t)$. This procedure can be justified term by term. However for the function $h(\rho)$ occurring in the correction term $O(h(\rho)/t)$ in (V.74) it is needed that for large t

$$\cdot \int_{r_o/\sqrt{Dt}} d\rho \; \rho^{n+2} \; e^{-\rho^2/4} \; h(\rho)/t \sim O(\tfrac{1}{t}) \; , \qquad (V.112)$$

which implies that the ρ integral exists if the lower limit tends to zero.

In this chapter we found the mode coupling predictions for $M^{(n)}(t)$ with the help of the relation (I.38b) and the result (V.45) for $\tilde{G}(k,t)$. To derive the relation (V.96) from (V.95) it is needed that the correction term of order $k^2h(\tau)$ in the expression (V.45) for $\tilde{G}(k,t)$ has the property that all derivatives of $h(\tau)$ for $\tau \to o$ exist and so $h(\tau)$ has to be an analytic function of τ . This requirement is rather similar to (V.112) for the function $h(\rho)$, which occurs in the correction term of $\tilde{\tilde{G}}(r,t)$.

Here we will calculate the functions u(s) and $u_p(s)$ defined in eq. (V.28) and (V.29).
The integral (V.28) for u(s) can be transformed into

$$\cdot \quad u(s) = (2\pi)^{-1} \int_0^1 dx\ (1-x^2) \int_{-\infty}^{+\infty} dy\ \{ \frac{y^2}{s-2xy+y^2} + \frac{y^2}{s+2xy+y^2} -2 \}\ .$$

The y integral can be performed by contour integration, yielding

$$\cdot \quad u(s) = \int_0^1 dx\ (1-x^2)\ (2x^2-s)\ (s-x^2)^{-\frac{1}{2}}$$

$$= \frac{1}{4}\ (s-2)\ \sqrt{s-1} - \frac{1}{4}\ s^2\ \tan^{-1} \frac{1}{\sqrt{s-1}}\ . \qquad (A.1)$$

In view of some transformations, to be carried out later, it is convenient to have an expression for u(s) in terms of hypergeometric functions.
This can be obtained by substitution of $y=x^2$ in (A.1), so that

$$\cdot \quad u(s) = s^{\frac{1}{2}} \int_0^1 dy\ y^{-\frac{1}{2}}\ (1-y)\ \{ -\ (1-y/s)^{\frac{1}{2}} + \tfrac{1}{2}\ (1-y/s)^{-\frac{1}{2}}\ \}\ . \qquad (A.2)$$

Using the integral representation of Gauss' hypergeometric function (Erdelyi 1953,1)

$$\cdot \quad u(s) = -\ \frac{2}{3}\ \sqrt{s}\ \{ 2\ {}_2F_1(\tfrac{1}{2},-\tfrac{1}{2};\tfrac{5}{2};\tfrac{1}{s}) -\ {}_2F_1(\tfrac{1}{2},\tfrac{1}{2};\tfrac{5}{2};\tfrac{1}{s})\ \}$$

$$= -\ \frac{2}{3}\ \sqrt{s}\ {}_2F_1(\tfrac{3}{2},-\tfrac{1}{2};\tfrac{5}{2};\tfrac{1}{s})\ . \qquad (A.3)$$

The last line is due to a property given in (Erdelyi 1953,2)

Next we calculate the function $u_p(s)$ for real values of p between zero and one. After carrying out the x integration in (V.29) one obtains

$$\cdot \quad u_p(s) = \frac{1}{\pi} \int_0^\infty dy\ y^p \left\{ -\frac{4}{3} - y^2 + \frac{1}{4} y\ (y^2+s) \log \frac{y^2+2y+s}{y^2-2y+s} \right\} . \qquad (A.4)$$

First we substitute in (A.4) $z = ye^{\pi i}$ and secondly $z = ye^{-\pi i}$, next we add up both expressions with te result

$$\cdot \quad \sin(p\pi)\ u_p(s) = \frac{1}{2\pi i} \int_{\Gamma_1+\Gamma_2} dz\ z^p \left\{ -\frac{4}{3} - z^2 - \frac{1}{4} z\ (z^2+s) \log \frac{z^2-2z+s}{z^2+2z+s} \right\} , \qquad (A.5)$$

where the contour Γ_1 is situated just above the branch cut of z^p , from $-\infty$ to o , and Γ_2 just below, from o to $-\infty$.
Apart from the branch cut along the negative real z axis, the integrand in (A.5) has two branch cuts along line segments from z_1 to z_3 and z_2 to z_4 respectively, where z_1 , ... , z_4 are logarithmic branch points, with $z_{1,2} = 1 \pm \sqrt{s-1}$ and $z_{3,4} = -1 \pm \sqrt{s-1}$. If we define Γ_3 and Γ_4 as closed contours around the upper and lower logarithmic branch cut respectively, both in the positive sense, we obtain, due to the behaviour of the integrand for $|z| \to \infty$, the following result

$$\cdot \quad \sin(p\pi)\ u_p(s) = \frac{-1}{2\pi i} \int_{\Gamma_3} dz\ z^p\ \frac{1}{4} z\ (z^2+s) \log \frac{z-z_1}{z-z_3} +$$

$$\frac{-1}{2\pi i} \int_{\Gamma_4} dz\ z^p\ \frac{1}{4} z\ (z^2+s) \log \frac{z-z_2}{z-z_4} .$$

Next we substitute $z = i\sqrt{s-1}+x\pm i\epsilon$ for Γ_3 and $z = -i\sqrt{s-1}+x\pm i\epsilon$ for Γ_4 , where $\epsilon \to o^+$, and x runs from -1 to +1 . The upper signs have to be taken along the upper sides of the branch cuts, the lower signs along the lower sides. This yields

$$\cdot \quad \sin(p\pi)\ u_p(s) = \tfrac{1}{2} \sin\frac{p\pi}{2} \int_{-1}^{+1} dx\ \left\{ (\sqrt{s-1}+ix)^{p+3} - s(\sqrt{s-1}+ix)^{p+1} \right\} ,$$

which gives the final result

$$\cdot \quad u_p(s) = \frac{s^{(p+4)/2}}{2\cos\frac{p\pi}{2}} \left[\frac{1}{p+4} \sin \left\{ (p+4) \tan^{-1}\frac{1}{\sqrt{s-1}} \right\} - \frac{1}{p+2} \sin \right.$$

$$\left. \left\{ (p+2) \tan^{-1}\frac{1}{\sqrt{s-1}} \right\} \right] . \qquad \text{(A.6)}$$

It is again convenient to have an expression for $u_p(s)$ in terms of hypergeometric functions, which can be obtained from the relation (Erdelyi 1953,3)

$$\cdot \quad {}_2F_1\left(\frac{p+1}{2}, -\frac{p-1}{2}; \frac{3}{2}; (\sin z)^2\right) = \frac{\sin(pz)}{p \sin z}$$

with the choice $\tan z = 1/\sqrt{s-1}$.

By using properties of contiguous functions (Erdelyi 1953,2,4,5) one finds

$$\cdot \quad u_p(s) = -\frac{(p+3)\ s^{(p+1)/2}}{3\cos\frac{p\pi}{2}}\ {}_2F_1\left(\frac{p+5}{2}, -\frac{p+1}{2}; \frac{5}{2}; \frac{1}{s}\right) . \qquad \text{(A.7)}$$

In this appendix we will calculate the functions $g(\rho)$ and $g_p(\rho)$ defined in (V.77) and (V.78).
The function $g(\rho)$ can be obtained from the following Fourier sine transform

$$I(\alpha,\beta,y) \equiv \int_0^\infty dx\,\sin(xy)\,x\,e^{-\alpha x^2}\;{}_1F_1(\beta;\tfrac{3}{2};x^2)\;, \tag{B.1}$$

which we will calculate first, for complex values of β with $\mathrm{Re}\beta<3/2$ and real values of α larger than one.
In order to calculate (B.1) we need the integral representation (Erdelyi 1953,6) valid for $\mathrm{Re}\beta<3/2$

$$\begin{aligned}{}_1F_1(\beta;\tfrac{3}{2};x^2) &= e^{x^2}\;{}_1F_1(\tfrac{3}{2}-\beta;\tfrac{3}{2};-x^2)\\ &= \frac{\Gamma(3/2)\;\Gamma(1-\beta)}{\Gamma(3/2-\beta)\;2\pi i}\int_0^{(1+)} du\;u^{\frac{1}{2}-\beta}\;(u-1)^{\beta-1}\;e^{(1-u)x^2}\;.\end{aligned} \tag{B.2}$$

The contour of integration is a loop starting (and ending) at u=o and encircling 1 once in the positive sense. After substitution of (B.2) into (B.1) the x integration can be carried out with the result

$$I(\alpha,\beta,y) = \frac{1}{4}\sqrt{\pi}\;y\;\frac{\Gamma(3/2)\;\Gamma(1-\beta)}{\Gamma(3/2-\beta)\;2\pi i}\int_0^{(1+)} du\;u^{\frac{1}{2}-\beta}\;v^{-3/2}\;e^{-y^2/(4v)}\;, \tag{B.3}$$

where $1/v = \alpha-1+u$.
Now the substitution $u = (\alpha-1)t\;/\;(\alpha-t)$, which leaves the contour invariant, yields

$$I(\alpha,\beta,y) = \frac{1}{4}\sqrt{\pi}\;y\;e^{-y^2/(4\alpha)}\;\frac{\alpha^{\beta-3/2}}{(\alpha-1)^{\beta}}\;\frac{\Gamma(3/2)\;\Gamma(1-\beta)}{\Gamma(3/2-\beta)\;2\pi i}$$
$$\int_0^{(1+)} dt\;t^{\frac{1}{2}-\beta}\;(t-1)^{\beta-1}\;\exp\{-\frac{y^2}{4\alpha(\alpha-1)}\;(1-t)\}\;. \tag{B.4}$$

Using the integral representation (B.2) again gives finally

$$I(a,\beta,y) = \frac{1}{4}\sqrt{\pi}\,\frac{a^{\beta-3/2}}{(a-1)^{\beta}}\;y e^{-y^2/(4a)}\;{}_1F_1(\beta;\tfrac{3}{2};\tfrac{-y^2}{4a(a-1)}) \;. \qquad (B.5)$$

The result (B.5) is in fact valid for all complex β, as can be shown by using a different integral representation for ${}_1F_1$.
For our purposes, $\mathrm{Re}\beta<3/2$ is sufficient.

The function $g(\rho)$ can be calculated from the result (B.5) and from (V.77).
By inserting for $w(\delta x^2)$ the expression (V.56) and applying the property

$$\tfrac{2}{3}y\;{}_1F_1(-\tfrac{1}{2};\tfrac{5}{2};y) = {}_1F_1(-\tfrac{1}{2};\tfrac{3}{2};y) - {}_1F_1(-\tfrac{3}{2};\tfrac{3}{2};y)\;, \qquad (B.6)$$

we arrive at the result

$$g(\rho) = -2\left\{\frac{1-\delta}{\pi\delta}\right\}^{\frac{1}{2}}\left\{\;{}_1F_1(-\tfrac{1}{2};\tfrac{3}{2};-\frac{\delta\rho^2}{4(1-\delta)}) + \right.$$

$$\left. -\;(1-\delta)\;{}_1F_1(-\tfrac{3}{2};\tfrac{3}{2};-\frac{\delta\rho^2}{4(1-\delta)}\right\}\;. \qquad (B.7)$$

The previous method fails in the calculation of $g_p(\rho)$, and we have not been able to calculate $g_p(\rho)$ in closed form.
Here we will derive a series expansion in powers of ρ, which converges absolutely for all values of ρ, and an asymptotic expansion for large values of ρ.
From (V.78) and (V.58) we have

$$g_p(\rho) = -\frac{32\,\Gamma((5+p)/2)\,\delta^{(1-p)/2}\,e^{\rho^2/4}}{3\,\pi^{3/2}\,(1-p^2)\,\rho}$$

$$\int_0^\infty dx\,\sin(x\rho)\,x^3\,e^{-x^2}\;{}_2F_2(\tfrac{5+p}{2},-\tfrac{1+p}{2};\tfrac{3-p}{2},\tfrac{5}{2};\delta x^2)\;. \qquad (B.8)$$

We insert the absolutely convergent expansion (V.32) for ${}_2F_2$ in (B.8), and integrate term by term using (Erdelyi 1954,2)

$$\cdot \quad \int_0^\infty dx \, \sin(x\rho) \, e^{-x^2} \, x^{2m+3} = \tfrac{1}{2} \, \Gamma(5/2) \, (5/2)_m \, \rho \, e^{-\rho^2/4} \, {}_1F_1(-m-1;\tfrac{3}{2};\rho^2/4) \; , \qquad \text{(B.9)}$$

where ${}_1F_1$ is a polynomial of degree (m+1) in ρ^2 .
The result is a hypergeometric series in two variables, ρ^2 and δ, where δ is a known quantity smaller than 1 (see (V.23)).
The most convenient representation for our purpose is

$$\cdot \quad g_p(\rho) = - \frac{4 \, \Gamma((5+p)/2) \, \delta^{(1-p)/2}}{\pi \, (1-p^2)} \sum_{m=o}^{\infty} \frac{(\frac{5+p}{2})_m \, (-\frac{1+p}{2})_m}{(\frac{3-p}{2})_m \, (\frac{3}{2})_m \, m!}$$

$${}_2F_1(m+\tfrac{5+p}{2},m-\tfrac{1+p}{2};m+\tfrac{3-p}{2};\delta) \; \{1-\frac{\rho^2}{4m+6}\} \; \{\frac{-\delta\rho^2}{4}\}^m \; . \qquad \text{(B.10)}$$

The asymptotic expansion of $g_p(\rho)$ can also be obtained from (B.8), if we extend in (B.8) the x integral from $-\infty$ to $+\infty$, write $\sin(x\rho) = \text{Im } e^{ix\rho}$ and substitute $x=z+\frac{1}{2}i\rho$. Because ${}_2F_2$ is an analytic funtion everywhere in the complex z plane, the integration path may be shifted such that $-\infty < z < +\infty$. For fixed ρ we may expand $(z+\frac{1}{2}i\rho)^3 \; {}_2F_2(\ldots;\delta(z+\frac{1}{2}i\rho)^2)$, occurring in the resulting expression, in powers of z and perform the z integrals. This yields an expansion of the form

$$\cdot \quad g_p(\rho) = \frac{2 \, \Gamma((5+p)/2) \, \delta^{(1-p)/2}}{3 \, \pi \, (1-p^2) \, \rho} \; \{ \sum_{m=o}^{\infty} \frac{(-)^m}{m!} \, (\frac{\partial}{\partial\rho})^{2m} \; \}$$

$$\rho^3 \; {}_2F_2(\tfrac{5+p}{2},-\tfrac{1+p}{2};\tfrac{3-p}{2},\tfrac{5}{2};\frac{-\delta\rho^2}{4}) \; . \qquad \text{(B.11)}$$

From the asymptotic expansion of ${}_2F_2$ as given in reference (Luke 1969) one can deduce the asymptotic expansion of $g_p(\rho)$ and we give only the first four terms

$$g_p(\rho) \sim \frac{\delta}{2(4+p)\cos(\pi p/2)\,\rho} \sum_{m=o}^{3} \frac{(-)^m}{m!} \left(\frac{\partial}{\partial\rho}\right)^{2m} \rho^{4+p} + O(\rho^{-2-p})$$

$$\sim \frac{\delta}{2(4+p)\cos(\pi p/2)} \rho^{3+p} \{ 1 + O(\rho^{-2}) \} . \qquad (B.12)$$

CONCLUSION

In this dissertation we have considered the derivation and possible extension of Fick's law.

In chapter I the quantities related to the diffusion of a tagged particle were introduced, and a formal microscopic expression for the propagator $\tilde{G}(k,t)$ of the diffusive mode was derived in terms of a projected k dependent velocity correlation function $\tilde{U}(k,t)$.
In addition we have given formal expressions for the time dependent diffusion coefficient $D^{(o)}(t)$, the time dependent super Burnett coefficient $D^{(2)}(t)$, and for the moments of displacement $M^{(n)}(t)$ and its cumulants $M_c^{(n)}(t)$.
Introduced in this chapter is also an essential concept for the derivation and extension of Fick's law, namely the hydrodynamic time scale, where we measure the time $\tau = Dk^2t$ in units $(Dk^2)^{-1}$, and where the wave number k can be treated as a small parameter.

The first step in the derivation and extension of Fick's law is an investigation of the limiting behaviour for long times of the diffusion coefficient $D^{(o)}(t)$, the super Burnett coefficient $D^{(2)}(t)$ and the intimately related velocity correlation function $\tilde{C}(t)$. This is done in the three subsequent chapters on the basis of kinetic theory for a system of hard spheres and hard disks at low densities.
The kinetic theory, derived in chapter II, uses standard diagrammatic techniques for many body problems, and is specialized to relatively low densities, where on the one hand explicit calculations are still feasible, while on the other hand the singular features of long memory effects are already present.
In chapters III and IV we have applie this kinetic theory respectively

to a system of hard spheres and hard disks and we have obtained explicit predictions for the long time behaviour of the velocity correlation function $\tilde{C}(t)$ in (III.24a) and (IV.90), for the diffusion coefficient $D^{(o)}(t)$ in (III.24b) and (IV.91) and for the super Burnett coefficient $D^{(2)}(t)$ in (III.55) and (IV.163). The latter two quantities are directly connected to the cumulants $M_c^{(2)}(t)$ and $M_c^{(4)}(t)$, as is shown in chapter I (I.44). These predictions will be compared with results from computer simulation experiments, as will be discussed below.

The first conclusion is that Fick's law does exist for three dimensional systems (since $D^{(o)}(t)$ tends to a constant for long times) and does not exist for two dimensions (since $D^{(o)}(t)$ diverges proportional to log t for $t\to\infty$). These results were already obtained in the literature (Dorfman 1970; Pomeau 1971).

Our second conclusion is that introducing a phenomenological super Burnett coefficient $D^{(2)}$ in constitutive relations like (I.29) does not yield a meaningful generalization of Fick's law, since $D^{(2)}(t)$ diverges for d=3 proportional to $-\sqrt{t}$ when t tends to infinity.

A further goal of the chapters III and IV is a confrontation of the predictions of the fundamental kinetic theory with the predictions of the more phenomenological mode coupling theory in their common region of applicability, i.e. low densities and hard sphere interactions. This is done because it is not possible to assess a priori the limits of applicability of the mode coupling formula for $\tilde{U}(k,t)$, apart from the restrictions to small wave numbers and large times.
To that aim we have calculated in chapter V, on the basis of the mode coupling theory for three dimensional systems, the velocity correlation function $\tilde{C}(t)$, see (V.70), and the cumulants $M_c^{(n)}(t)$, see (V.103), which are for n=2 and 4 directly related to $D^{(o)}(t)$ and

$D^{(2)}(t)$, given in (V.102) and (V.109), and we have seen that the results agree with those of chapter III.
The agreement between kinetic theory and mode coupling theory for $\tilde{C}(t) = \tilde{U}(o,t)$ has already been discussed in the literature (Dorfman 1972). By our method we have extended the comparison by considering $D^{(2)}(t)$, which is related to the second derivative of $\tilde{U}(k,t)$ with respect to k at $k=o$ and fixed values of t . This can be derived by means of the equations of chapter I, and explicit details are given in a separate publication (De Schepper 1974).

We conclude from our results for $D^{(o)}(t)$ and $D^{(2)}(t)$ that the mode coupling theory describes correctly the leading singularities of $\tilde{U}(k,t)$ or $U(k,z)$ for low densities and hard sphere systems for large t or small z up to order k^2 inclusive.

There is a good indication from kinetic theory that the leading singularities of $\tilde{U}(k,t)$ or $U(k,z)$ are predicted correctly from the mode coupling theory up to *all* orders in k . That is to say that the expression (V.108) for $D^{(2j)}(t)$ can be verified from kinetic theory for all values of j ($j=0,1,2,\ldots$). Such an investigation would involve in kinetic theory the calculation of n point velocity correlation functions, which in diagrammatic language can be represented by attaching n crosses to the diagrams of figure 1 on page 46. The explicit calculations then are rather similar to those of $D^{(2)}(t)$, but we have not studied those diagrams in detail.

The agreement between the kinetic theory and the mode coupling theory in their common region of validity is considered as partial evidence for the correctness of the mode coupling theory for general fluid densities and for more general short ranged intermolecular interactions, the reason being that the phenomenological arguments for the derivation of the mode coupling formula nowhere imply any restriction on densities or intermolecular potentials.

As the next point we will briefly discuss the comparison between the theoretical predictions for $\tilde{C}(t)$ and $D^{(2)}(t)$ and the results from computer experiments for two and three dimensional hard sphere systems. An extensive discussion on this comparison has been given by Wood (Wood 1974), both for the predictions for the velocity correlation function, which were already known in the literature (Dorfman 1970; Ernst 1970), as well as for the super Burnett coefficient.

In making the comparison there exist two serious problems. The first one is the time scale on which the asymptotic predictions become dominant, which requires the times to be sufficiently long. The second one is the finite size effect in actual computer calculations, which requires the times to be sufficiently short. Both restrictions may shrink the region, where a decent comparison can be made, to zero.

The first problem does not seem to be serious for the velocity correlation function $\tilde{C}(t)$, the short time behaviour of which is expected to decay exponentially in a few mean free times. On the basis of our low density kinetic theory we obtained in section IV*c*, an estimate of $9t_o$ before the asymptotic behaviour is dominant.
However for the super Burnett coefficient, $D^{(2)}(t)$, it takes a considerable time before the short time behaviour has reached its constant value. This was discussed in chapter III (compare (III.37)) and chapter IV (compare (IV.114)) in connection with the prediction for $D^{(2)}(t)$ from the Lorentz-Boltzmann equation, here denoted by $D^{(2)}_{LB}(\underline{t})$.
Consequently the estimated time ($\sim 15t_o$) for which our asymptotic theory becomes dominant at low densities, is considerably larger than for $\tilde{C}(t)$.
For fluid densities we have no means of estimating the times for which the asymptotic contributions to $\tilde{C}(t)$ and $D^{(2)}(t)$ become dominant, since

the methods applied in section IV*c* break down as soon as the mean free path l_o is approximately equal or smaller than the sphere or disk diameter σ . In two dimensional systems this is the case for reduced densities $n^{\star} > 1/5$ and in three dimensional systems for $n^{\star} > 1/10$, as can be seen from table I on page 154.

The second problem is the effect of the finite size of the system, which become appreciable at times of the order of the acoustic traversal time t_a , indicated by the vertical arrow (↑) in figure 14,15,16,17. The quantity t_a is the time a sound wave needs to traverse the system and may be considered as a measure for the finiteness of the volume. By comparing figure 14,15,16 and 17, one sees that, given the number of particles, the effect of the finite size is much more pronounced in three than in two dimensional systems.

After these preliminaries we discuss the actual comparison for the velocity correlation function $\tilde{C}(t)$ in both two and three dimensions, where the leading asymptotic behaviour is given by $\tilde{C}(t) \approx d_o/t^{d/2}$ (d=2,3). This expression for $\tilde{C}(t)$ is given for d=3 and low densities in (III.24a) and for d=3 and fluid densities in (V.70). For d=2 we only have eq. (IV.90), which is valid for low densities.
The two dimensional results for $\tilde{C}(t)$ at fluid densities have been obtained either from the mode coupling theory to which we will return below, or from an extension of the low density kinetic theory, as given by Dorfman and Cohen (Dorfman 1970).
The higher correction terms in (III.24a) and (V.70) (d=3) turn out to be numerically insignificant. A discussion of the two dimensional correction terms in (IV.90) will be given below.
Wood studied quantitatively the finite size effects for $\tilde{C}(t)$, which are quite large for times of the order of, or larger than the acoustic traversal time, both for d=2 and d=3 . Such finite size effects can be explained from the mode coupling theory (cfr. (V.1)) by keeping the

volume V finite and summing over all allowed (discrete) wave numbers, instead of introducing Fourier integrals. Then the agreement between theory and experiment for $\tilde{C}(t)$ turns out to be very well, both for two and three dimensional systems.

Next we consider the super Burnett coefficient in three dimensions. In figure 14 and 15 the computer results for the time dependent super Burnett coefficient $D^{(2)}(t)$ are given at two densities $n^* = V_o/V = 1/10$ and $n^* = V_o/V = 1/3$ for a system of 4000 hard spheres. In these figures t_o is the actual mean free time, which is equal to the mean free time at low densities, used in chapter III (III.6), divided by χ_E , where χ_E is the radial distribution function for hard spheres at contact. The function $\tilde{D}^{(2)}(t)$ is a dimensionless quantity defined by

$$\tilde{D}^{(2)}(t) = \frac{(\beta m)^2}{t_o^3} D^{(2)}(t) .$$

The function $\tilde{D}^{(2)}_{LB}(t)$ drawn in figure 14 and 15 (the upper curve) represents the theoretical prediction from the Lorentz-Boltzmann equation, which is qualitatively given by the expression (III.37b). It describes correctly the actual *short* time behaviour of $D^{(2)}(t)$ up to 10 mean free times.
The lower curve in figure 14 and 15 is our theoretical prediction (V.109) for $D^{(2)}(t)$, where the Enskog values of the transport coefficients are used (Chapman 1960) and where only the leading term proportional to $-\sqrt{t}$ is taken into account. The correction terms proportional to $t^{1/4}$, $t^{1/8}$, ... in (V.109), turn out to be numerically small for the densities considered here.
A quantitative study of the finite size effects is still lacking for the three dimensional $D^{(2)}(t)$. The problems connected with finite size effects and with the time scale for the validity of our asymptotic theory seem to indicate that the region, where a decent comparison between theoretical and computer results can be made, has shrunken

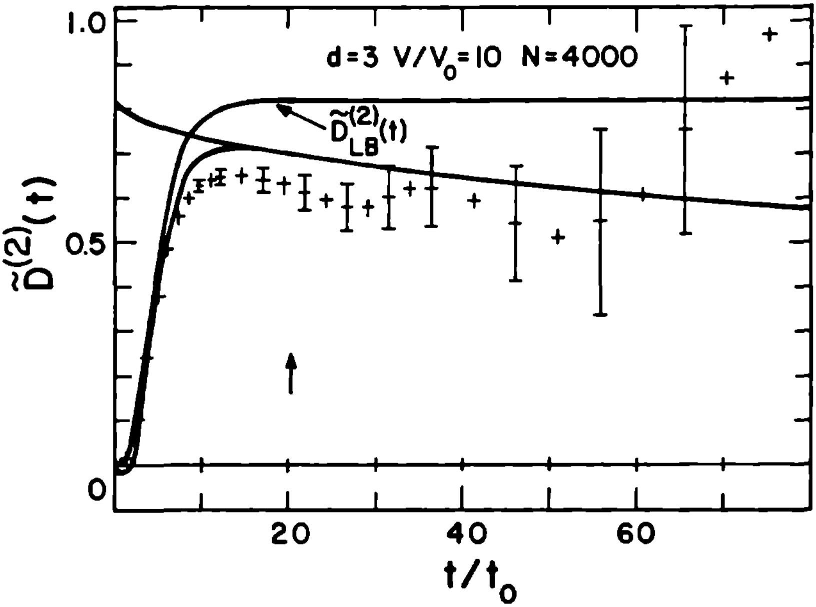

figure 14 : The time dependent super Burnett coefficient $\tilde{D}^{(2)}(t)$ according to Wood (Wood 1974) for a three dimensional system of 4000 hard spheres at a reduced density $n^{*} = 1/10$. The acoustic traversal time t_a is $21t_o$ (see arrow). The upper curve represents the prediction from the Lorentz-Boltzmann equation $(\tilde{D}^{(2)}_{LB}(t))$, the lower curve that from the mode coupling theory.

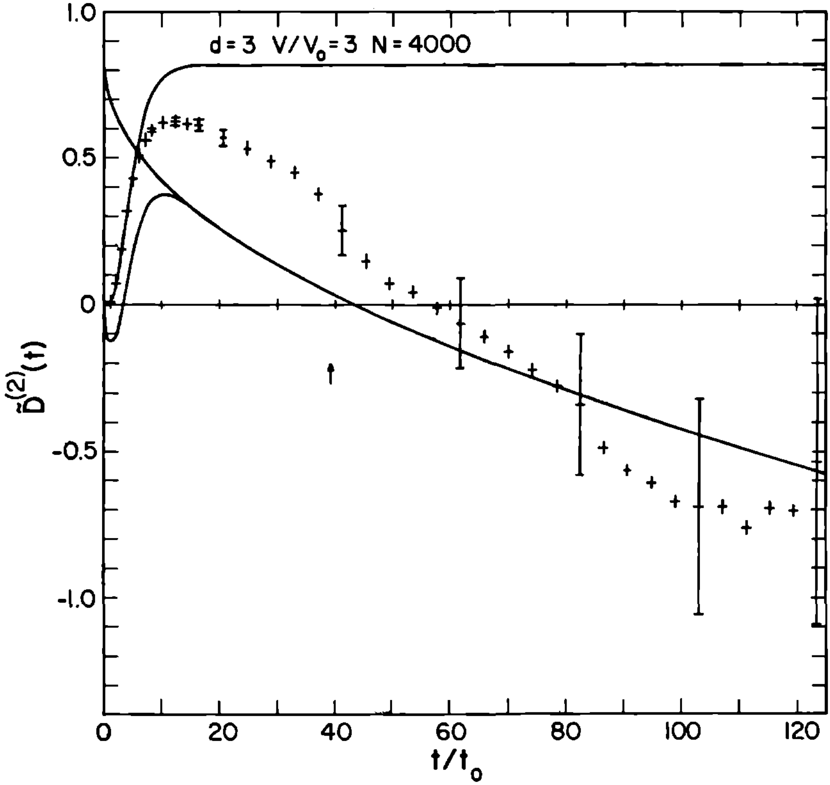

figure 15 : The time dependent super Burnett coefficient $\widetilde{D}^{(2)}(t)$ according to Wood (Wood 1974) for a three dimensional system of 4000 hard spheres at $n^{☆} = 1/3$ and with $t_a = 39t_o$.

to zero, so that the comparison for the three dimensional super Burnett coefficient $D^{(2)}(t)$, is inconclusive.
In any case, the computer results supply some evidence that the time dependent diffusion coefficient $D^{(2)}(t)$ for d=3 does not tend to a constant for long times.

For a two dimensional system of hard disks the comparison with our theoretical results for $D^{(2)}(t)$ is necessarily restricted to low densities ($n^{*} \lesssim 1/10$), as discussed in section IV*c*.
We have obtained a relation of the form (IV.163)

$$D^{(2)}(t) = D^{(2)}_{LB} + e_1 t + e_2 t \log(t/t_o) + \ldots .$$

The results from computer calculations are shown in figure 16, where $n^{*} = 1/10$ and in figure 17, where $n^{*} = 1/3$. The reduced super Burnett coefficient is defined, similarly as above, by

$$\tilde{D}^{(2)}(t) = \frac{(\beta m)^2}{t_o^3} D^{(2)}(t) ,$$

where t_o is the actual mean free time.
The short time behaviour is described correctly by the Lorentz-Boltzmann prediction $D^{(2)}_{LB}(t)$, which is qualitatively given by the expression (IV.114). It tends to a constant for $t\to\infty$, denoted by $D^{(2)}_{LB}$.
In figure 16 the acoustic traversal time is equal to 62 mean free times. In figure 17 it is $104 t_o$. Although finite size effects for these systems are not yet studied, it is reasonable to suppose that they are insignificant for times considerable smaller than the acoustic traversal time.
The dashed curve in figure 16 represents our theoretical prediction (IV.163) for $D^{(2)}(t)$, if all transport coefficients in e_1 (compare (IV.20) and (IV.164)) are replaced by their Enskog values. At this density ($n^{*} = 1/10$) the Enskog values differ only a few percent from

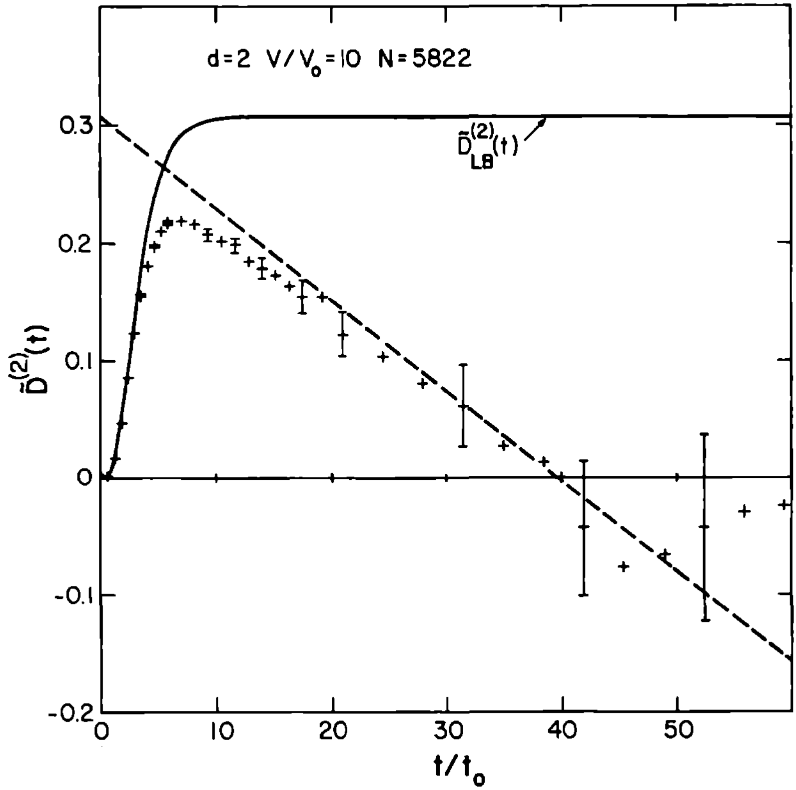

figure 16 : The time dependent super Burnett coefficient $\tilde{D}^{(2)}(t)$ according to Wood (Wood 1974) for a two dimensional system of 5822 hard disks at $n^{*} = 1/10$ and with $t_a = 62t_o$ (off the scale).

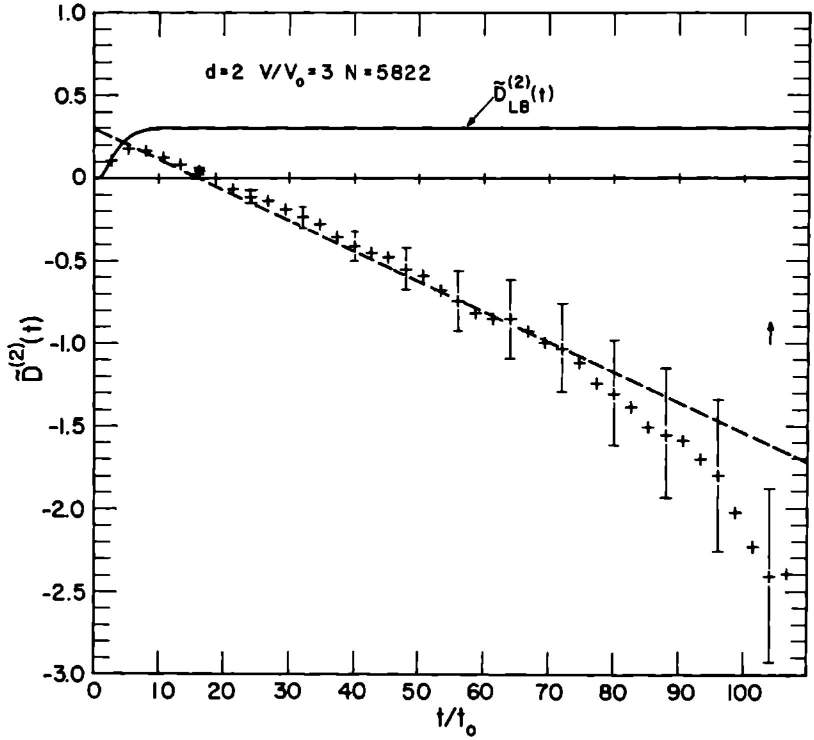

figure 17 : The time dependent super Burnett coefficient $\tilde{D}^{(2)}(t)$ according to Wood (Wood 1974) for a two dimensional system of 5822 hard disks at $n^{\star} = 1/3$ and with $t_a = 104t_o$.

their Boltzmann value, and the actual mean free time equals within 15% the value of t_o given by (IV.6).
As we have seen already in section IV*c* (compare (IV.169,173)) the term $e_2 t \log(t/t_o)$ is negligable for this density and the times considered in figure 16. The dashed curve in figure 16 therefore, is a straight line with negative slope. We conclude from figure 16 that the agreement between theory and experiment is quite good in this case.

An extension of our results to fluid densities on the basis of the two dimensional mode coupling theory has not been worked out in this dissertation, due to some conceptual difficulties in this theory to which we will return below.
However, one can *formally* follow the same procedure for solving the two dimensional mode coupling equation as was given in chapter V for the three dimensional case. In doing so one obtains results for the long time behaviour of $\tilde{C}(t)$ and $D^{(2)}(t)$, which are indentical in form to our low density results (IV.166) and (IV.167), but the transport coefficients appearing in these expressions are replaced by the so called bare transport coefficients (compare the discussion below (V.7)).
If one identifies the bare transport coefficients with those obtained from Enskog's theory (Chapman 1960) for a dense gas of hard spheres, and restricts one self to the first terms, i.e. $\tilde{C}(t) \approx d_o/t$ and $D^{(2)}(t) \approx D^{(2)}_{LB} + e_1 t$, the agreement between theory and computer experiments is very good. This can be seen e.g. from figure 17, where $\tilde{D}^{(2)}(t)$ is plotted as a function of time at a reduced density $n^* \doteq 1/3$.

The conceptual difficulties in the two dimensional mode coupling theory occur if one includes the higher correction terms in $\tilde{C}(t)$ and $D^{(2)}(t)$, i.e.

. $\tilde{C}(t) \approx d_o/t + d_1/t \log(t/t^*_o)$

$$\cdot \quad D^{(2)}(t) \approx D_{LB}^{(2)} + e_1 t + e_2 t \log(t/t_o^{\star}) ,$$

where we have written $t_o^{\star}$ instead of t_o , to indicate that the cut-off time $t_o^{\star}$ occurs in the theory as an undetermined parameter, which is in general not equal to the mean free time.

If time becomes sufficiently long the higher correction terms start to dominate over the preceding terms.

For the times and densities of interest in computer experiments, the term $d_1/t \log(t/t_o^{\star})$ in the velocity correlation function is insignificant for all reasonable choices of $t_o^{\star}$, due to the fact that the ratio d_1/d_o is small for all densities.

For the super Burnett coefficient $D^{(2)}(t)$ the correction term $e_2 t \log(t/t_o^{\star})$ becomes quite large for densities $n^{\star} > 1/5$, and one has to choose $t_o^{\star}$ equal to 30-50 mean free times in order to fit the computer data with the theory. One may conclude from this that the higher correction terms present in $\widetilde{C}(t)$ and $\widetilde{D}^{(2)}(t)$ require a much longer time to build up to their full asymptotic strength as given by $d_1/t \log(t/t_o)$ and $e_2 t \log(t/t_o)$. An indication that the time scale on which the higher correction terms become important is much larger than the time on which the first terms (i.e. d_o/t and $e_1 t$) become dominant is given by the estimates in section IV*c* from our low density kinetic theory.

However the precise nature of these time scales at fluid densities is not yet understood.

Finally we have considered the generalization of Fick's law for three dimensional systems, which have been given in chapter V on the basis of the mode coupling theory. The basic idea was that the macroscopic quantities, which in general depend on two variables (e.g. (k,z) , (k,t) , (r,t)), basically depend only on *one* dimensionless quantity (e.g. ζ , κ , τ , ρ) which is of order unity, if the variables are chosen in their hydrodynamic regions. This dimensionless quantity is either a combination of wave numbers k and frequencies z ($\zeta = z/(Dk^2)$) , .

or wave numbers k and times t ($Dk^2t = \tau = \kappa^2$) or of positions r and times t ($\rho^2 = r^2/(Dt)$). The dependence on the other variable (e.g. k or t^{-1}) is weak, so that this quantity can be treated as a small expansion parameter.

In this way we have obtained explicit expressions for the hydrodynamic propagators $G(k,z)$ in (V.39), $\tilde{G}(k,t)$ in (V.45) and $\tilde{\tilde{G}}(r,t)$ in (V.74), and for the "projected" velocity correlation functions $U(k,z)$ in (V.27), $\tilde{U}(k,t)$ in (V.44) and $\tilde{\tilde{U}}(r,t)$ in (V.76). The function $\tilde{U}(k,t)$ appears as memory function in the generalized diffusion equation (I.60), namely $\partial\tilde{G}(k,t)/\partial t = -k^2 \int_0^t dt' \, \tilde{U}(k,t') \, \tilde{G}(k,t-t')$.

From eq. (I.64) and (V.47) one can also straightforwardly derive the k dependent velocity correlation function $\tilde{C}(k,t)$.

Our method also allows us to generalize Fick's law in the form (I.27), namely $\partial\tilde{G}(k,t)/\partial t = -k^2 \, \tilde{D}(k,t) \, \tilde{G}(k,t)$, and obtain an explicit expression for the generalized diffusion coefficient $\tilde{D}(k,t)$. This will be discussed in a separate publication.

The experimental verification of our results can in principle be studied in incoherent neutron scattering, where one measures the scattering function $S(k,\omega)$, which is the Fourier transform of $\tilde{G}(k,t)$. Some results in this direction have been reported in (Andriesse 1970), but the experimental accuracy does not seem good enough to justify any conclusions.

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SAMENVATTING

In dit proefschrift wordt het zelfdiffusieproces in een klassiek gas- of vloeistofsysteem theoretisch bestudeerd.

Bij dit verschijnsel is men geïnteresseerd in de gemiddelde beweging van een van de deeltjes in het systeem, in het bijzonder vraagt men naar de kans om zo'n deeltje op een bepaalde tijd op een bepaalde plaats aan te treffen als bekend is, dat het zich aanvankelijk op een andere plaats bevond. Zulke verdelingsfunkties in gassen of vloeistoffen voldoen volgens de irreversibele thermodynamica in het algemeen aan hydrodynamische vergelijkingen, geldig voor grote tijden en langzame ruimtelijke variaties. Voor het zelfdiffusieproces is er één zo'n relatie, bekend als de diffusievergelijking of de wet van Fick. Deze wet bevat de diffusiecoëfficient als fenomenologische parameter.

We bestuderen de afleiding en mogelijke uitbreiding van de diffusievergelijking zowel in twee- als in driedimensionale systemen met behulp van twee theorieën:

- de fundamentele kinetische theorie voor een systeem van harde bollen bij lage dichtheden en
- de fenomenologische "mode coupling" theorie, welke niet beperkt is tot lage dichtheden of harde bollen interakties.

Het belang van een dergelijke studie, op basis van juist deze theorieën, blijkt uit recente computerexperimenten, waarin wordt aangetoond, dat de snelheidscorrelatiefunktie van een deeltje in een harde bollen systeem een langzaam vervallende funktie van de tijd is. Dit onverwachte resultaat is in tegenspraak met oudere theorieën, zoals de Boltzmann vergelijking, die een snel verval van de snelheids-

correlatiefunktie voorspellen, maar wordt wel verklaard door de kinetische en de "mode coupling" theorie.
De tweevoudige aanpak is gekozen, enerzijds om sommige computerresultaten te kunnen verklaren, die verkregen zijn voor verdunde en verdichte systemen van harde bollen en harde schijven, anderzijds om de fenomenologische "mode coupling" theorie, die van groot belang is bij de bestudering van niet evenwichtseigenschappen nabij het kritische punt, te verifiëren met behulp van de fundamentele kinetische theorie. Dit laatste wordt gedaan door voorspellingen van beide theorieën te vergelijken in hun gemeenschappelijk geldigheidsgebied (nl. lage dichtheden).

Enkele consequenties van het langzame verval van de snelheidscorrelatiefunktie voor de hydrodynamica van het zelfdiffusieproces worden in dit proefschrift bestudeerd,met de volgende resultaten.
De wet van Fick bestaat niet voor tweedimensionale systemen, zoals reeds bekend in de literatuur.
De wet van Fick bestaat wel in drie dimensies maar kan niet op eenvoudige wijze worden uitgebreid door het invoeren van één of meer fenomenologische hogere orde diffusiecoëfficienten.
De voorspellingen van beide bovengenoemde theorieën voor de gemiddelde tweede en vierde macht van de verplaatsing van een gemerkt deeltje komen met elkaar overeen in hun gemeenschappelijk geldigheidsgebied.
Deze theoretische voorspellingen stemmen in redelijke mate overeen met resultaten van computerexperimenten.
Een generalizatie van de diffusievergelijking voor minder lange tijden en minder langzame ruimtelijke variaties wordt verkregen op basis van de "mode coupling" theorie in driedimensionale systemen.

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STELLINGEN

I

Het verschil tussen de resultaten voor de tijdafhankelijke super Burnett coëfficiënt, die voorkomt in de diffusievergelijking van tweedimensionale systemen, zoals gegeven in dit proefschrift en door Keyes en Oppenheim, is terug te voeren op inconsistente benaderingen in het werk van laatstgenoemde auteurs.

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II

Als de relatie voor het lange-tijdsgedrag van de snelheidscorrelatiefunktie C(t) in twee dimensies, namelijk $C(t) \sim [(D+\nu)t]^{-1}$, wordt opgevat als een zelfconsistente vergelijking voor de tijdafhankelijke diffusiecoëfficiënt $D(t) = \int_0^t dt' \, C(t')$, volgt voor asymptotisch lange tijden dat $C(t) \sim [t\sqrt{\log t}]^{-1}$.
Dit resultaat kan, met behulp van hersommatietechnieken, voor lage dichtheden worden afgeleid uit de kinetische theorie gegeven in dit proefschrift.

T.E. Wainwright, B.J. Alder en D.M. Gass,
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M.H. Ernst, E.H. Hauge en J.M.J. van Leeuwen,
Phys. Rev. A4 (1971) 2055.

III

Het gedrag van de licht- of neutron-verstrooiïngsfunktie $S(k,\omega)$ kan niet, tot op willekeurige orde, worden beschreven met behulp van dispersierelaties.

J.A. McLennan,
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Physica 75 (1974) 1.

Het asymptotisch lange-tijdsgedrag van golfvektor- en tijdafhankelijke correlatiefunties, zoals de gegeneraliseerde diffusiecoefficient $D(k,t)$ of de intermediaire verstrooiingsfunktie $G(k,t)$, voor een vaste waarde van k ongelijk aan nul, kan in het algemeen niet verkregen worden uit mode koppeling theorieen of theorieen gebaseerd op fluctuerende hydrodynamica

D Bedeaux en P Mazur,
Physica 73 (1974) 431

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Hoofdstuk V van dit proefschrift

V

Als de Fourier-sinus getransformeerde van een funktie $f(x)$ wordt gedefinieerd als $\int_0^\infty dx \sin(xy) f(x)$, en de confluente hypergeometrische funktie wordt geschreven als ${}_1F_1(\beta, \alpha, x)$, dan kan voor alle reele waarden van a en b waarvoor $a > b > 0$, voor alle complexe waarden van β en voor alle positieve gehele getallen m en n, de Fourier-sinus getransformeerde van de funktie $x^{2n-1} \exp(-ax^2)\ {}_1F_1(\beta, \frac{3}{2} + n-m, bx^2)$ worden uitgedrukt als een eindige som van termen, elk gelijk aan het produkt van een polynoom in y de funktie $\exp(-y^2/(4a))$ en een confluente hypergeometrische funktie met argument $-by^2 / (4a(a\ b))$ Voor n=1 en m=1 is de getransformeerde gelijk aan

$$\tfrac{1}{4}\sqrt{\pi}\, a^{\beta-3/2}\, (a-b)^{-\beta}\, y \exp\left(\frac{-y^2}{4a}\right)\ {}_1F_1\left(\beta, \frac{3}{2}, \frac{-by^2}{4a(a-b)}\right)$$

Hoofdstuk V, appendix B, van dit proefschrift

VI

In het triangulaire "wind-tree" model bewegen puntdeeltjes zich zonder onderlinge interaktie tussen willekeurig geplaatste niet bewegende harde verstrooiers, bestaande uit congruente gelijkzijdige driehoeken De zijden van al deze driehoeken zijn evenwijdig, de grootte van de snelheid van alle puntdeeltjes is gelijk en de richting is evenwijdig aan één van de zijden van een driehoek

Dit systeem is niet ergodisch.

VII

In niet-ergodische systemen met harde pit interakties convergeert de gemiddelde vrije tijd tussen twee botsingen in het algemeen niet naar de inverse botsingsfrequentie.

VIII

In de Wilson theorie van kritische verschijnselen mag een "fixed point" met twee eigenwaarden groter dan 1 niet zonder meer met een trikritisch punt geïdentificeerd worden.

E.K. Riedel en F.J. Wegner,
Phys. Rev. Lett. 29 (1972) 349.

IX

In het Gaussisch model neemt de renormalisatiegroepvergelijking in termen van $\chi(k)$ slechts in schijn een eenvoudige vorm aan, omdat de renormalisatie vergelijking, die dan weliswaar lineair is, beschouwd moet worden in een niet-lineaire oplossingsruimte.

Th. Niemeyer en J.M.J. van Leeuwen,
Phys. Lett. 41A (1972) 211.

J.J. González, E.H. Hauge en P.C. Hemmer
preprint (1974).

X

Het door Kosterlitz beschreven ferromagnetische XY model lijkt geschikt om te worden toegepast op de thermodynamica van een systeem van lijnvortices in uniform roterend Helium II.

J.M. Kosterlitz,
J. Phys. C7 (1974) 1046

W.F. Vinen,
in Progress in low temperature physics III, C.J. Gorter ed.,
N.H.P.C. (Amsterdam 1961)

J.S. Langer en J.D. Reppy,
in Progress in low temperature physics VI, C.J. Gorter ed.,
N.H.P.C. (Amsterdam 1970).

Omscholing als middel ter bestrijding van de werkloosheid is ineffectief zolang kandidaten één tot twee jaar op toelating moeten wachten.

cijfer voor de omscholingscursussen aan het Centrum voor
Vakopleiding van Volwassenen te Nijmegen

Nijmegen, 24 januari 1975 Ignatz de Schepper